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PRACTICE PAPERS

JEE FINAL TOUCH · Class 11
Last 3 Years Chapterwise Questions

CHEMISTRY
today

India's #1 CHEMISTRY MONTHLY FOR JEE (Main & Advanced) & PMTs

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CBSE Board
Class XII

Competition Corner

Concept Map

NCERT Corner

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Chemistry Musing

CHEMISTRY tOday

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Need to Rejuvenate Universities

Every year, in many parts of India, on Saraswathi Pooja at the end of Navarathra, all men, women and children keep the books for Pooja and start their studies all over again, first starting with alphabets.

Universities, particularly the old ones, have reached their height after years of struggle. It is now the duty of all associated with centres of higher learning to keep up the position. But there are many problems. There are ways of solving any problem. Let us take the inspiration from our national laboratories, our scientists who could send rockets to the moon and nuclear explosions.

Right from the highest level to the lowest, it is a single chain. We start from each part.

It is human resources that comes first. Contact between teachers and students is most important. Time stands still when clearing the doubts of students. Whether it is the classroom or laboratory, students should be aware that help is nearby. Interaction between students and teachers comes first. Students should be very respectful to the teachers and the teachers, affectionate and kind to the students.

The library should be common. It should have the latest journals and books from the lowest level to the highest. Students should be encouraged to sit in the library and use it. By having books of general interest to the students, cross-current books such as applications of group-theory biology to statistical applications to various fields should be available.

Instead of dividing the money for various departments, they should be pooled. Computers, X-ray diffractometers, spectrometers, ranging from X-ray to infrared, mass spectrometers, chromatography should be common facilities, each under a specialist who is continuing to do research in the field.

Inter-university interactions is the same as pooling.

Conferences should be common to all departments and weekly lectures should be common and every person can attend. But the specialists have to participate.

Let us study the first class centres of learning where there is no politics.

Most of our top universities are more than a century old. All of us have a stake in the progress of education in our country and a duty to support the universities.

Anil Ahlawat
Editor

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM
Set 9

JEE MAIN/PMTS

1. Which of the following order is incorrect?
   (a) $NH_3 < PH_3 < AsH_3 < SbH_3$
      : Reducing character
   (b) $Li < Be < B < C$: 1st Ionisation energy
   (c) $Al_2O_3 < MgO < Na_2O < K_2O$: Basic character
   (d) $La^{3+} > Ce^{3+} > Pm^{3+} > Yb^{3+}$: Ionic radius

2. 1.5% solution of urea is isotonic with a 5.25% solution of a substance in the same solvent. The molar mass of the substance is
   (a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
   (c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}

3. What will be the major product of the following reaction?

   (a)

   (b)

   (c)

   (d)
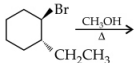
4. Na_2O_2
   (a) is diamagnetic in nature
   (b) is a salt of dibasic acid H_2O_2
   (c) oxidises Cr^{3+} (green) to CrO_4^{2-} (yellow)
   (d) all of these.

5. A white crystalline solid 'X' dissolves in hot water. On passing H_2S in this solution, a black precipitate 'Y' is obtained which dissolves completely in hot HNO_3. On adding a few drops of conc. H_2SO_4 a white precipitate 'Z' is obtained. Identify 'X'.
   (a) $BaSO_4$ (b) $SrSO_4$
   (c) $PbCl_2$ (d) $CdSO_4$

6. The equilibrium constant for the reaction $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ is 4.0 at 25°C. Calculate the weight of ethyl acetate that will be obtained when 120 g of acetic acid reacts with 92 g of ethanol.
   (a) 120 g (b) 162 g (c) 85 g (d) 117 g

COMPREHENSION

Redox reactions play an important role in chemistry and biology. The values of standard redox potentials ($E°$) of two half-cell reactions decide the path in which the reaction is expected to proceed. A simple example is a 'Daniel cell' in which zinc goes into solution and copper gets deposited. On the basis of the given data, answer the following questions.

$I_2 + 2e^- \longrightarrow 2I^-$; $E° = 0.54$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E° = 0.77$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; $E° = 1.23$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$; $E° = 1.36$

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$; $E° = 1.50$
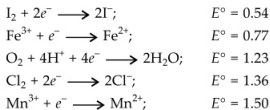
7. Which of the following statements is correct?
   (a) Cl^- is oxidised by O_2.
   (b) Fe^{2+} is oxidised by iodine.
   (c) I^- is oxidised by chlorine.
   (d) Mn^{2+} is oxidised by chlorine.

8. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
   (a) O_2 oxidises Mn^{2+} to Mn^{3+}
   (b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
   (c) Fe^{3+} oxidises H_2O to O_2
   (d) Mn^{3+} oxidises H_2O to O_2.

INTEGER VALUE

9. The number of monochlorinated products possible for free radical chlorination of 2, 2-dimethylbutane is

10. Total number of Lewis acids among the following is
    BF_3, H_3PO_4, NH_3, SiF_4, CH_3COOH, $NaOH$, CO_2, HCl, SO_3

SOME BASIC CONCEPTS OF CHEMISTRY

1. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is **(Integer Type, 2012)**

2. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is
   (a) 1.78 M   (b) 2.00 M
   (c) 2.05 M   (d) 2.22 M   **(2011)**

3. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is **(Integer Type, 2011)**

4. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to **(Integer Type, 2011)**

STRUCTURE OF ATOM

5. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at –73°C is M times that of the de Broglie wavelength of Ne at 727°C. M is

   (Integer Type, 2013)

6. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom [a_0 is Bohr radius]

   (a) $\dfrac{h^2}{4\pi^2 ma_0^2}$ (b) $\dfrac{h^2}{16\pi^2 ma_0^2}$

   (c) $\dfrac{h^2}{32\pi^2 ma_0^2}$ (d) $\dfrac{h^2}{64\pi^2 ma_0^2}$ **(2012)**

7. The maximum number of electrons that can have principal quantum number, $n = 3$, and spin quantum number, $m_s = -\dfrac{1}{2}$, is

   (Integer Type, 2011)

8. The work function (φ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
φ(eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(Integer Type, 2011)

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

9. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?

$$^{63}_{29}\text{Cu} + ^{1}_{1}\text{H} \rightarrow 6\,^{1}_{0}n + \alpha + 2\,^{1}_{1}\text{H} + X$$
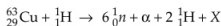
(Integer Type, 2012)

CHEMICAL BONDING AND MOLECULAR STRUCTURE

10. The shape of XeO_2F_2 molecule is
    (a) trigonal bipyramidal
    (b) square planar   (c) tetrahedral
    (d) see-saw.   **(2012)**

STATES OF MATTER

11. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the PV vs $1/V$ plot is shown below. The value of the van der Waals constant a (atm litre^2 mol^{-2}) is

    (a) 1.0   (b) 4.5   (c) 1.5   (d) 3.0
    (2012)

12. According to kinetic theory of gases
    (a) collisions are always elastic
    (b) heavier molecules transfer more momentum to the walls of the container
    (c) only a small number of molecules have very high velocity
    (d) between collisions, the molecules move in straight lines with constant velocities.

    (2011)

13. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to

    (Integer Type, 2011)

THERMODYNAMICS

14. The standard enthalpies of formation of $CO_{2(g)}$, $H_2O_{(l)}$ and glucose$_{(s)}$ at 25°C are – 400 kJ/mol, – 300 kJ/mol and – 1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is
    (a) + 2900 kJ   (b) – 2900 kJ
    (c) – 16.11 kJ   (d) + 16.11 kJ   **(2013)**

Paragraph for Question Nos. 15 and 16

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.
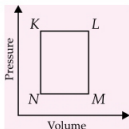
15. The pair of isochoric processes among the transformation of states is
    (a) K to L and L to M (b) L to M and N to K
    (c) L to M and M to N (d) M to N and N to K

    (2013)

16. The succeeding operations that enable this transformation of states are
    (a) heating, cooling, heating, cooling
    (b) cooling, heating, cooling, heating
    (c) heating, cooling, cooling, heating
    (d) cooling, heating, heating, cooling.

    (2013)

17. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is(are) correct? [Take ΔS as change in entropy and w as work done]
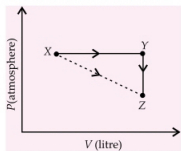
    (a) $\Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z}$
    (b) $w_{X \to Z} = w_{X \to Y} + w_{Y \to Z}$
    (c) $w_{X \to Y \to Z} = w_{X \to Y}$
    (d) $\Delta S_{X \to Y \to Z} = \Delta S_{X \to Y}$ **(2012)**

18. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C $\equiv$ C bond in C_2H_2. That energy is (take the bond energy of a C – H bond as 350 kJ mol^{-1})
    $2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$; $\Delta H = 225$ kJ mol^{-1}
    $2C_{(s)} \longrightarrow 2C_{(g)}$; $\Delta H = 1410$ kJ mol^{-1}
    $H_{2(g)} \longrightarrow 2H_{(g)}$; $\Delta H = 330$ kJ mol^{-1}
    (a) 1165   (b) 837
    (c) 865   (d) 815   **(2012)**
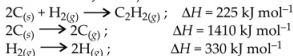
19. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?
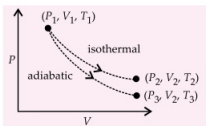
    (a) $T_1 = T_2$ (b) $T_3 > T_1$
    (c) $w_{isothermal} > w_{adiabatic}$
    (d) $\Delta U_{isothermal} > \Delta U_{adiabatic}$ **(2012)**

20. Match the transformations in Column I with appropriate options in Column II.

Column I		Column II	
A.	$CO_{2(s)} \longrightarrow CO_{2(g)}$	p.	Phase transition
B.	$CaCO_{3(s)} \longrightarrow$ $CaO_{(s)} + CO_{2(g)}$	q.	Allotropic change
C.	$2H^\bullet \longrightarrow H_{2(g)}$	r.	ΔH is positive
D.	$P_{(white, solid)} \longrightarrow$ $P_{(red, solid)}$	s.	ΔS is positive
		t.	ΔS is negative

(2011)

21. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1 M) is $1/100^{th}$ of that of a strong acid (HX, 1 M), at 25°C. The K_a of HA is
(a) 1×10^{-4}
(b) 1×10^{-5}
(c) 1×10^{-6}
(d) 1×10^{-3}

(2013)

22. The thermal dissociation equilibrium of $CaCO_{3(s)}$ is studied under different conditions.
$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
For this equilibrium, the correct statement(s) is (are)
(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of the catalyst, if any.
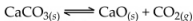
(2013)

23. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is
(a) 1.1×10^{-11}
(b) 1.1×10^{-10}
(c) 1.1×10^{-12}
(d) 1.1×10^{-9}

(2013)
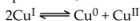
24. The equilibrium,
$$2Cu^I \rightleftharpoons Cu^0 + Cu^{II}$$
in aqueous medium at 25°C shifts towards the left in the presence of
(a) NO_3^-
(b) Cl^-
(c) SCN^-
(d) CN^-

(2011)

25. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl [K_{sp}(CuCl) = 1.0×10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of x is

(Integer Type, 2011)

26. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
(a) HNO_3, NO, NH_4Cl, N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2

(2012)

27. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively
(a) redox reaction; –3 and –5
(b) redox reaction; +3 and +5
(c) disproportionation reaction; –3 and +5
(d) disproportionation reaction; –3 and +3

(2012)

28. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is

(Integer Type, 2011)

29. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are
(a) II, III haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

(2011)

30. With respect to graphite and diamond, which of the statement(s) given is(are) correct?
(a) Graphite is harder than diamond.
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C – C bond order than diamond.

(2012)
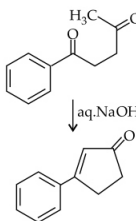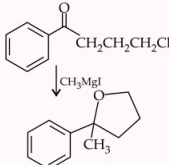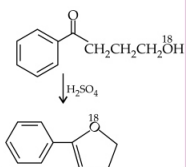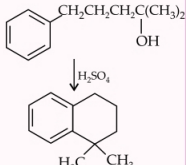
31. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to
(a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
(c) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
(d) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations. (2013)

32. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is(are)
(a) sp and sp^3
(b) sp and sp^2
(c) only sp^2
(d) sp^2 and sp^3 (2012)

33. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II.

	Column I		Column II
A.	aq.NaOH	p.	Nucleophilic substitution
B.	CH₂CH₂CH₂Cl, CH₃MgI	q.	Electrophilic substitution
C.	H₂SO₄	r.	Dehydration
D.	CH₂CH₂CH₂C(CH₃)₂ OH, H₂SO₄	s.	Nucleophilic addition
		t.	Carbanion
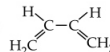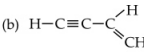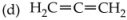
(2011)

34. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is
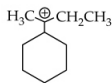
35. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are)

(a) $H_2C=CH-CH=CH_2$ type structure

(b) $H-C\equiv C-CH=CH_2$

(c) $H_2C=C=O$

(d) $H_2C=C=CH_2$

(2011)

HYDROCARBONS

36. Among P, Q, R and S, the aromatic compound(s) is(are)

(a) P (b) Q
(c) R (d) S
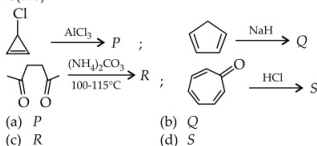
(2013)

37. The number of optically active products obtained from the complete ozonolysis of the given compound is

$$CH_3-CH=CH-\overset{CH_3}{\underset{H}{C}}-CH=CH-\overset{H}{\underset{CH_3}{C}}-CH=CH-CH_3$$
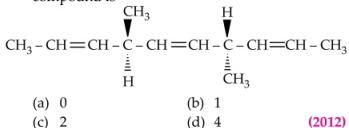
(a) 0   (b) 1
(c) 2   (d) 4   **(2012)**

38. Which of the following molecules, in pure form, is(are) unstable at room temperature?

(a)   (b)

(c)   (d)
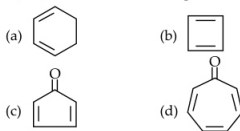
(2012)

Paragraph for Question Nos. 39 and 40

An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.

$$\underset{(C_6H_{10})}{P} \xrightarrow[\text{(iii) acid}]{\substack{\text{(i) dil. } H_2SO_4/HgSO_4 \\ \text{(ii) } NaBH_4/\text{ethanol}}} Q$$

$$Q \xrightarrow[\substack{\text{(ii) } O_3 \\ \text{(iii) } Zn/H_2O}]{\substack{\text{(i) conc. } H_2SO_4 \\ \text{(catalytic amount)} \\ (-H_2O)}} 2 \; \underset{H_3C}{\overset{O}{\underset{}{\parallel}}} \!\!\! C \!-\! CH_3$$
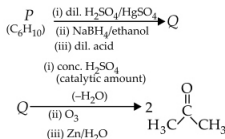
39. The structure of compound P is

(a) $CH_3CH_2CH_2CH_2-C\equiv C-H$

(b) $H_3CH_2C-C\equiv C-CH_2CH_3$

(c) $\underset{H_3C}{\overset{H_3C}{>}}H-C-C\equiv C-CH_3$

(d) $\underset{H_3C}{\overset{H_3C}{\underset{H_3C}{>}}}C-C\equiv C-H$
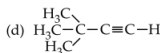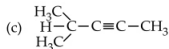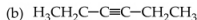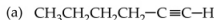
(2011)

40. The structure of the compound Q is

(a) $\underset{H_3C}{\overset{H_3C}{>}}H-\overset{OH}{\underset{H}{C}}-\overset{}{\underset{}{C}}-CH_2CH_3$

(b) $\underset{H_3C}{\overset{H_3C}{>}}C-\overset{OH}{\underset{H}{C}}-CH_3$

(c) $\underset{H_3C}{\overset{H_3C}{>}}H-C-CH_2CHCH_3$ with OH

(d) $CH_3CH_2CH_2\overset{OH}{\underset{}{C}}HCHCH_3$
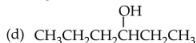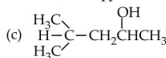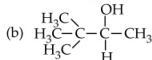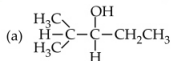
(2011)

41. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentyl-hexane using alcoholic KOH is

(Integer Type, 2011)

42. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is

$$CH_3CH_2\overset{CH_3}{\underset{H}{C}}CH_2CH_3$$
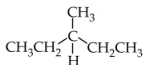
(Integer Type, 2011)

1. **(8) :** 29.2% w/w of HCl,
⇒ Mass of HCl = 29.2 g
⇒ Mass of solution = 100 g

d = 1.25 g/mL, Mol. wt. of HCl = 36.5 g mol^{-1}
Volume of solution = 100 g/1.25 g mL^{-1} = 80 mL

$$\text{Molarity} = \frac{w/\text{mol.wt}}{\text{Volume of solution}} \times 1000$$

$$= \frac{(29.2/36.5)}{80} \times 1000 = 10 \text{ M}$$

Using $M_1V_1 = M_2V_2$

$10 \times V_1 = 0.4 \times 200 \;\; \Rightarrow \;\; V_1 = \frac{200 \times 0.4}{10} = 8 \text{ mL}$

2. **(c) :** Total mass of solution
= 1000 + 120 = 1120 g
Total volume of solution

$$= \frac{\text{Mass}}{\text{Density}} = \frac{1120}{1.15} = 973.91 \text{ mL}$$

$$M = \frac{w \times 1000}{\text{Mol.wt} \times V(\text{mL})} = \frac{120 \times 1000}{60 \times 973.91} = 2.05 \text{ M}$$

3. **(5) :** $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

So, number of NaBr molecules = 5

4. **(6) :** $[Cr(H_2O)_5Cl]Cl_2 + 2AgNO_3 \longrightarrow 2AgCl$
$+ [Cr(H_2O)_5Cl](NO_3)_2$

Number of ionisable chloride ions in complex $[Cr(H_2O)_5Cl]Cl_2$ = 2.

Millimoles = Molarity × Volume (mL) × 2
= 0.01 × 30 × 2 = 0.6

Therefore, required Ag$^+$ ions = 0.6 millimoles
According to,
Millimoles = Molarity × V(mL)
0.6 = 0.1 × V; V = 6 mL

5. **(5) :** $\lambda = \dfrac{h}{\sqrt{2m \times K.E.}}$

$$\frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{m_{Ne} \times K.E._{Ne}}{m_{He} \times K.E._{He}}}$$

$$\frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{m_{Ne} \times T_{Ne}}{m_{He} \times T_{He}}} \qquad [\because K.E. \propto T]$$

$$= \sqrt{\frac{20 \times 1000}{4 \times 200}}$$

$$\frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{20000}{800}} = 5$$

$\lambda_{He} = 5 \lambda_{Ne}$

6. **(c) :** For Bohr orbit, angular momentum is

$$mvr_n = \frac{nh}{2\pi} \; ; \quad v = \frac{nh}{2\pi m r_n} \qquad \ldots \text{(i)}$$

Kinetic energy, $K.E. = \dfrac{1}{2}mv^2 \qquad \ldots \text{(ii)}$

By putting the value of v from (i) to (ii),

$$K.E. = \frac{1}{2} m \times \frac{n^2 h^2}{4\pi^2 m^2 r_n^2} = \frac{n^2 h^2}{8\pi^2 m r_n^2}$$

For second Bohr orbit, $n = 2$

$r_n = a_0 \times n^2$ (a_0 = Bohr radius)

$r_n = 4 \, a_0$

$$K.E. = \frac{(2)^2 h^2}{8\pi^2 m (4a_0)^2}$$

Thus, $K.E. = \dfrac{h^2}{32\pi^2 m a_0^2}$

7. **(9)** : For principal quantum number ($n = 3$)

Number of orbitals = $n^2 = 9$

Total no. of electrons = $2n^2 = 18$

So, number of electrons with $m_s = -\dfrac{1}{2}$ will be 9.

8. **(4)** : The energy associated with incident photon

$$= \frac{hc}{\lambda}$$

$$\therefore \quad E = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}}$$

$$E \text{ (in eV)} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.6 \times 10^{-19}} = 4.141 \text{ eV} \approx 4 \text{ eV}$$

Photoelectric effect can take place only if $E_{\text{photon}} \geq \phi$

Thus, Li, Na, K and Mg can show photoelectric effect. So, the answer is 4.

9. **(8)** : $^{63}_{29}Cu + ^{1}_{1}H \rightarrow 6\,^{1}_{0}n + ^{4}_{2}He(\alpha) + 2\,^{1}_{1}H + ^{52}_{26}X$

Atomic number 26 represents Fe which belongs to group 8.

Alternatively, $Z = 26$

Electronic configuration $= 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 4s^2 \, 3d^6$

Thus, element X belongs to d-block and for d-block,

Group number = electrons in $(n - 1)$ subshell + number of electrons in valence shell

= 6 + 2 = 8

10. **(d)**: Xe is in sp^3d hybrid state in XeO_2F_2 with 1 lone pair of electrons.
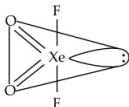
Geometry : Trigonal bipyramidal
Shape : See-saw

11. **(c)** : van der Waals equation is

$$\left(P + \frac{a}{V^2} \right)(V - b) = RT$$

As given that $b = 0$

$$PV + \frac{a}{V} = RT \quad \text{or} \quad PV = RT - \frac{a}{V}$$

Comparing with $y = mx + c$

Intercept (c) $= RT$

Slope (m) $= -a$

Slope $= \dfrac{y_2 - y_1}{x_2 - x_1} = \dfrac{20.1 - 21.6}{3 - 2} = -1.5$

Thus, $a = 1.5$

12. **(a, b, c, d)** : All of these are correct.

13. **(7)** : For any ideal gas, $PV = nRT$

$0.32 \times V = 0.1 \times 0.0821 \times 273$

$V = 7$ litre
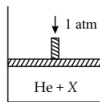
For He, $n = 0.1$, $P = 1 - 0.68 = 0.32$ atm, $V = ?$, $T = 273$ K (unknown compound X will not follow ideal gas equation)

14. **(c)** : $C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$

$\Delta H_c^\circ = \Sigma \Delta H_f^\circ \text{(products)} - \Sigma \Delta H_f^\circ \text{(reactants)}$

$= [6 \times \Delta H_f^\circ (CO_2) + 6 \times \Delta H_f^\circ (H_2O)] - [\Delta H_f^\circ (C_6H_{12}O_6)$
$\qquad\qquad\qquad\qquad\qquad\qquad + 6 \times \Delta H_f^\circ (O_2)]$

$= [6 \times (-400) + 6 \times (-300)] - [-1300 + 6(0)]$

$= (-2400 - 1800) - (-1300) = -4200 + 1300$

$= -2900$ kJ/mol

The standard enthalpy of combustion per gram of

glucose $= \dfrac{-2900}{180} = -16.11$ kJ/g

15. **(b)**: In isochoric process, volume is constant.

16. **(c)** :
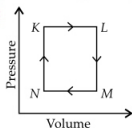
$K \rightarrow L$; heating, isobaric

$L \rightarrow M$; cooling, isochoric

$M \rightarrow N$; cooling, isobaric

$N \rightarrow K$; heating, isochoric

17. **(a, c)** : As ΔS does not depend on path and only depends on initial and final stages *i.e.*, it is a state function thus,

$\Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z}$

and $\Delta S_{Y \to Z}$ is not zero thus

$\Delta S_{X \to Z} \neq \Delta S_{X \to Y}$

As we know that work is not a state function and depends on path,

Thus, $w_{X \to Z} \neq w_{X \to Y} + w_{Y \to Z}$

$\quad w_{X \to Y} = PdV \qquad (\because P \text{ is constant})$

$\quad w_{Y \to Z} = 0 \qquad (\because V \text{ is constant})$

$w_{X \to Y \to Z} = w_{X \to Y} + w_{Y \to Z}$

As $w_{Y \to Z} = 0$, hence $w_{X \to Y \to Z} = w_{X \to Y}$

18. **(d):** Ethyne molecule breaks as

$C_2H_{2(g)} \longrightarrow 2C_{(g)} + 2H_{(g)}$ ... (i)

Given equations are

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$; $\Delta H = 225$ kJ/mol ... (ii)

$2C_{(s)} \longrightarrow 2C_{(g)}$; $\Delta H = 1410$ kJ/mol ... (iii)

$H_{2(g)} \longrightarrow 2H_{(g)}$; $\Delta H = 330$ kJ/mol ... (iv)
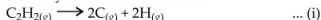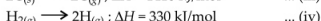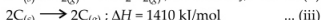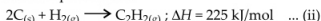
Eqn. (i) can be obtained by adding equation (iii) and (iv) and then subtracting eq. (ii).

ΔH for (i) $= \Delta H_{(iii)} + \Delta H_{(iv)} - \Delta H_{(ii)}$

$\qquad = 1410 + 330 - 225 = 1515$ kJ/mol

Equation (i) involves breaking of 2 C – H bonds and 1 C $\equiv$ C bond, thus

ΔH of eq. (i) = 2 × bond energy of C – H bonds + bond energy of C $\equiv$ C bond

$1515 = 2 \times 350 + C \equiv C$ bond energy

Bond energy of C $\equiv$ C bond = 815 kJ/mol

19. **(a, c, d):** (a) $T_1 = T_2$ as the process is isothermal. Hence, (a) is correct.

(b) $T_3 < T_1$ because cooling takes place on adiabatic expansion. Hence (b) is incorrect.

(c) $w_{isothermal} > w_{adiabatic}$ because area under the isothermal curve is greater than under the adiabatic curve. Hence (c) is correct.

(d) $\Delta U_{adiabatic} = -ve$ because when adiabatic expansion occurs, internal energy decreases. Thus, $\Delta U_{isothermal} > \Delta U_{adiabatic}$. Hence (d) is correct.

20. **(A) → (p, r, s)**

$CO_{2(s)} \longrightarrow CO_{2(g)}$

(i) It is an example of phase transition.

(ii) Conversion of solid into gas i.e., sublimation, which is endothermic, therefore, ΔH = positive

(iii) For solid $\longrightarrow$ gas ΔS = positive

because, $\Delta S = S_{(g)} - S_{(s)}$ $\quad S_{(g)} > S_{(s)}$

(B) → (r, s)

$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$
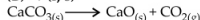
Thermal decomposition of $CaCO_3$ is endothermic process so, ΔH = positive.

When any product is gas and reactant is solid then, ΔS = positive.

(C) → (t)

$2H^{\bullet} \longrightarrow H_{2(g)}$
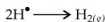
Conversion of radical in molecular form is exothermic, $\Delta H = -ve$. Formation of bond between two particles decreases the disorder. So, $\Delta S = -ve$.

(D) → (q, r, t)

It is an allotropic change. By heating white P to 573 K, it is converted to highly ordered polymeric red P.

So, $\Delta H = +ve$; $\Delta S = -ve$

21. **(a):** Rate with respect to weak acid

$R_1 = k[H^+]_{weak\ acid}$

and rate with respect to strong acid

$R_2 = k[H^+]_{strong\ acid}$

$\therefore \quad \dfrac{R_1}{R_2} = \dfrac{k[H^+]_{weak\ acid}}{k[H^+]_{strong\ acid}} = \dfrac{1}{100}$

$\therefore \quad [H^+]_{weak\ acid} = \dfrac{1}{100} \times 1 = 0.01$ M

$\qquad\qquad (\because [H^+]_{strong\ acid} = 1\ M)$

$\underset{1-0.01\approx 1 \quad\quad 0.01 \quad\quad 0.01}{HA \quad \rightleftharpoons H^+ + A^-}$

$K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{0.01 \times 0.01}{1} = 1 \times 10^{-4}$

22. **(a,b,d):** $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

The equilibrium constant (K) is independent of the initial amount of $CaCO_3$ whereas is independent of pressure of CO_2. ΔH is independent of catalyst and it depends on temperature.

23. **(b):** $\underset{\quad\quad\quad\quad 2S \quad\quad S}{Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}}$

$\underset{\quad\quad\quad 0.1 \quad\quad 0.1}{AgNO_3 \longrightarrow Ag^+ + NO_3^-}$
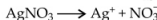
$[CrO_4^{2-}] = S$, $[Ag^+] = [2S + 0.1] \approx 0.1$ M

$\qquad [\because Ag_2CrO_4$ is sparingly soluble salt]

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$[CrO_4^{2-}] = \dfrac{K_{sp}}{[Ag^+]^2} = \dfrac{1.1 \times 10^{-12}}{(0.1)^2} = 1.1 \times 10^{-10}$ mol L^{-1}

$S = 1.1 \times 10^{-10}$ mol L^{-1}

24. **(b, c, d):** Cu^{2+} ion will react with CN^- and SCN^- forming $[Cu(CN)_4]^{3-}$ and $[Cu(SCN)_4]^{3-}$ leading the reaction to the backward direction.

$Cu^{2+} + 2CN^- \longrightarrow 2Cu^+ + (CN)_2$

$Cu^+ + CN^- \longrightarrow CuCN$

$CuCN + 3CN^- \longrightarrow [Cu(CN)_4]^{3-}$

$Cu^{2+} + 4SCN^- \longrightarrow [Cu(SCN)_4]^{3-}$

Cu^{2+} also combines with Cl^- to form $CuCl_2$ which reacts with Cu to produce CuCl pushing the reaction in the backward direction.

$$CuCl_2 + Cu \longrightarrow 2CuCl$$
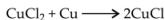
25. (7) : Let the solubility of AgCl is a mol litre^{-1}

$$AgCl \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{Cl^-}; \quad CuCl \rightleftharpoons \underset{b}{Cu^+} + \underset{b}{Cl^-}$$

$\therefore$ K_{sp} of AgCl = $[Ag^+][Cl^-]$

$1.6 \times 10^{-10} = a\,(a+b)$ ...(i)

Similarly, K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.0 \times 10^{-6} = b\,(a+b)$ ...(ii)

On solving (i) and (ii), we get

$\dfrac{a}{b} = 1.6 \times 10^{-4}$ or $a = 1.6 \times 10^{-4} \times b$

Substituting the value of a in eqn. (i),

$1.6 \times 10^{-10} = 1.6 \times 10^{-4}\, b\,(1.6 \times 10^{-4}\, b + b)$

$\Rightarrow 10^{-6} = b^2\,(1.6 \times 10^{-4} + 1)$ $[\because\ 1.6 \times 10^{-4} <\!\!<\!\!< 1]$

$\Rightarrow b = 10^{-3} \Rightarrow a = 1.6 \times 10^{-7}$

$[Ag^+] = 1.6 \times 10^{-7}$; $\therefore$ $x = 7$

26. (b): Let the oxidation state of nitrogen is x.

$HNO_3 \Rightarrow +1 + x + 3(-2) = 0 \Rightarrow x - 5 = 0$

$\Rightarrow x = +5$

$NO \Rightarrow x + 1(-2) = 0 \Rightarrow x = +2$

$NH_4Cl \Rightarrow x + 4(+1) + (-1) = 0 \Rightarrow x + 4 - 1 = 0$

$\Rightarrow x = -3$

N_2 (elementary state) $\Rightarrow x = 0$

Decreasing order of oxidation state is

$$\begin{array}{cccc} HNO_3, & NO, & N_2, & NH_4Cl \\ +5 & +2 & 0 & -3 \end{array}$$

27. None is correct.

White phosphorus dissolves in NaOH on boiling in inert atmosphere.

$$\underset{}{P_4 + 3NaOH + 3H_2O} \longrightarrow \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$
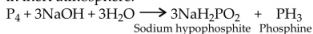
Let the oxidation state of phosphorus be x.

$PH_3 \Rightarrow x + 3 = 0 \Rightarrow x = -3$

In NaH_2PO_2,

$+1 + 2(+1) + x + 2(-2) = 0$

$+3 + x - 4 = 0 \Rightarrow x = +1$

Thus, the given reaction is disproportionation as oxidation state changes from 0 to -3 and $+1$. But none of the given options is correct.

28. (5) :
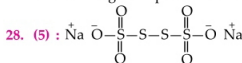
The oxidation number of each of the S atoms linked with each other in the middle is zero while that of each of the remaining two S atoms is $+5$. Difference in oxidation number = 5

29. (d) : In haematite (Fe_2O_3) oxidation number of iron,

$2x + 3 \times (-2) = 0$, $x = +3$

Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3.

Therefore, oxidation number of iron in FeO,

$x - 2 = 0 \Rightarrow x = +2$

Oxidation number of iron in Fe_2O_3,

$2x + 3 \times (-2) = 0$; $x = +3$

30. (b, d) : Diamond is the hardest substance known and C – C bond length is 1.54 Å in diamond. It is non-conductor of electricity. While in graphite, after sp^2 hybridisation one electron is free and it overlaps with another electron to form π-bond, thus bond length in graphite is shorter (1.42 Å) and bond order is higher than diamond. The π-electron is free to move thus, graphite is good conductor of electricity but it is bad conductor of heat whereas diamond has the highest thermal conductivity of any known substance.

31. (a) :
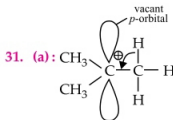
In *tert*-butyl cation, carbon bearing positive charge has one vacant p-orbital. Hence, it is $\sigma \rightarrow p$ (empty) electron delocalisation.
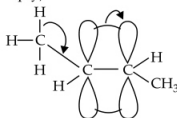
In 2-butene, it is $\sigma \rightarrow \pi^*$ electron delocalisation.

32. (b): Allene, $\underset{sp^2}{H_2C} = \underset{sp}{C} = \underset{sp^2}{CH_2}$

33. (A) $\rightarrow$ (r, s, t); (B) $\rightarrow$ (p, s); (C) $\rightarrow$ (r, s); (D) $\rightarrow$ (q, r)

(A)
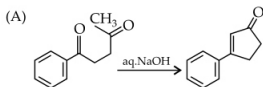
Aldol condensation is an example of nucleophilic addition reaction.

(carbanion)
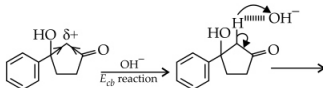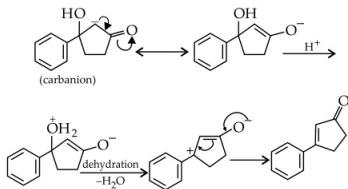
dehydration
−H₂O

Hence, nucleophilic addition, formation of carbanion, dehydration takes place. So, (A) ⟶ (r, s, t)

(B)
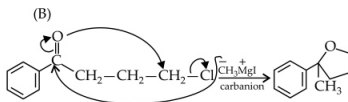
(i) It is an example of nucleophilic addition reaction *i.e.*, reaction between Grignard reagent and keto group is nucleophilic addition.
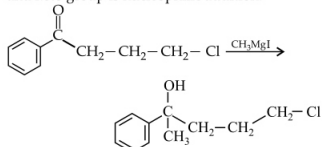
(ii) Now reaction is nucleophilic substitution.

So, (B) ⟶ (p, s)

(C)
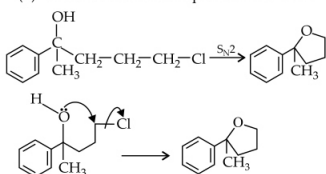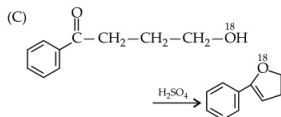
In this reaction nucleophilic addition and dehydration take place.

Nucleophilic addition
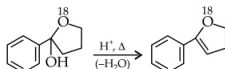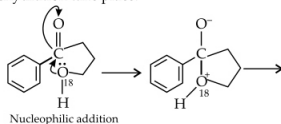
So, it is an example of nucleophilic addition reaction and dehydration also takes place. So, (C) ⟶ (r, s)

(D)
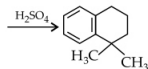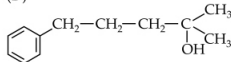
It is Friedel — Craft reaction which is electrophilic substitution.
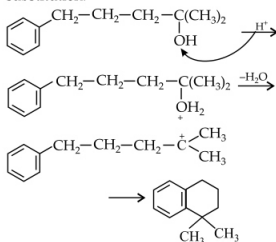
This reaction is an example of dehydration and electrophilic substitution. So, (D) ⟶ (q, r)

34. (6) :
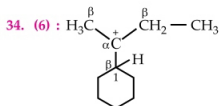
∴ No. of hyperconjugation structures involving C − H bond = 6

35. (b, c) : Along C—C single bond, conformations are possible in butadiene in which all the atoms may not lie in the same plane.

36. (a,b,c,d) : (i) [cyclopropenyl structure] —Cl $\xrightarrow{AlCl_3}$ [cyclopropenyl cation] $\overset{\oplus}{}$ $AlCl_4^{\ominus}$
(P) Aromatic

(ii) [cyclopentadiene] $\xrightarrow{NaH}$ [cyclopentadienyl anion] $\overset{\oplus}{Na}$ + H₂
(Q) Aromatic

(iii) [diketone] $\xrightarrow[100\text{-}115°C]{(NH_4)_2CO_3}$ [pyrrole structure]
(R) Aromatic

(iv) [cyclohexadienone] =O $\xrightarrow{HCl}$ [$\overset{\oplus}{}$—OH]$Cl^{\ominus}$
(S) Aromatic

37. (a) :

$CH_3CH=CH-\overset{CH_3}{\underset{H}{C}}-CH=CH-\overset{H}{\underset{CH_3}{C}}-CH=CHCH_3$

$\downarrow 3O_3$

$CH_3CH\overset{O}{\underset{O}{|}}CH-\overset{CH_3}{\underset{H}{C}}-CH\overset{O}{\underset{O}{|}}CH-\overset{H}{\underset{CH_3}{C}}-CH\overset{O}{\underset{O}{|}}CHCH_3$

$\downarrow Zn/H_2O$

$CH_3CHO + OHC-\overset{CH_3}{\underset{H}{C}}-CHO + OHC-\overset{CH_3}{\underset{H}{C}}-CHO$

$+ CH_3CHO$

All are optically inactive.

38. (b, c) : (b) and (c) are planar molecules and contain 4π electrons hence, antiaromatic and unstable while (a) is a non-planar and contains 4π electrons hence, non-aromatic and (d) is planar and contains 6π electrons hence, aromatic and stable at room temperature. Antiaromatic compounds are even less stable than the corresponding non-planar 4π electron system.

39. (d)

40. (b)

Note :

$\overset{H_3C}{\underset{H_3C}{\overset{|}{C}}}\overset{H_3C}{\underset{}{}}-C\equiv C-H \xrightarrow[HgSO_4]{dil.\ H_2SO_4}$ $\overset{H_3C}{\underset{H_3C}{\overset{H_3C}{C}}}-\overset{O}{\overset{||}{C}}-CH_3$
(P)

$\xrightarrow[dil.\ H^+]{NaBH_4/EtOH}$ $\overset{H_3C}{\underset{H_3C}{\overset{H_3C}{C}}}-\overset{OH}{\underset{}{CH}}-CH_3 \xrightarrow[conc.\ H_2SO_4]{\Delta}$
(Q)

$\overset{H_3C}{\underset{H_3C}{C}}=C\overset{CH_3}{\underset{CH_3}{}} \xrightarrow{O_3,\ Zn/H_2O} \overset{H_3C}{\underset{H_3C}{C}}=O + O=C\overset{CH_3}{\underset{CH_3}{}}$
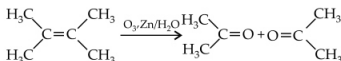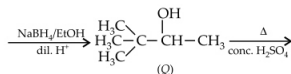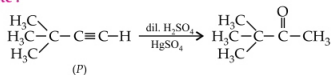
41. (5) : Total no. of alkenes will be = 5
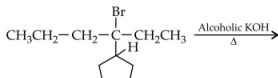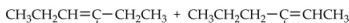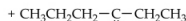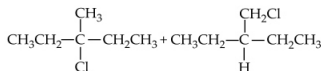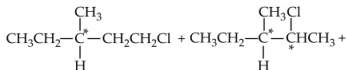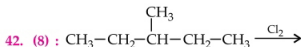
$CH_3CH_2-CH_2-\overset{Br}{\underset{H}{C}}-CH_2CH_3 \xrightarrow[\Delta]{Alcoholic\ KOH}$

3-Bromo-3-cyclopentylhexane

$CH_3CH_2CH=C-CH_2CH_3$ + $CH_3CH_2CH_2-C=CHCH_3$
(E + Z isomers) [cyclopentyl]   (E + Z isomers) [cyclopentyl]

$+ CH_3CH_2CH_2-C-CH_2CH_3$
(Only one isomer) [cyclopentyl]

42. (8) : $CH_3-CH_2-\overset{CH_3}{\underset{}{CH}}-CH_2-CH_3 \xrightarrow{Cl_2}$

$CH_3CH_2-\overset{CH_3}{\underset{H}{\overset{*}{C}}}-CH_2CH_2Cl$ + $CH_3CH_2-\overset{CH_3Cl}{\underset{*}{\overset{*}{C}}}-CHCH_3$ +

$CH_3CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3$ + $CH_3CH_2-\overset{CH_2Cl}{\underset{H}{C}}-CH_2CH_3$

Total = 2 + 4 + 1 + 1 = 8

1. Which of the following compounds involve sp^3d^3 hybridisation?
   (a) SF_6 (b) IF_7 (c) PF_5 (d) $SnCl_4$

2. Plot of Maxwell's distribution of velocities is given below :
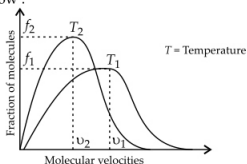
Which of the following is correct about this plot?
   (a) $T_1 < T_2$ (b) $f_1 > f_2$
   (c) $\upsilon_1 < \upsilon_2$ (d) None of these.

3. The donor atoms in EDTA are
   (a) Two N and two O   (b) Two N and four O
   (c) Four N and two O   (d) Three N and Three O.

4. The reaction,
   $C_6H_5ONa + CO_2 + H_2O \rightarrow C_6H_5OH + NaHCO_3$
   suggests that
   (a) phenol is a stronger acid than carbonic acid
   (b) carbonic acid is a stronger acid than phenol
   (c) water is a stronger acid than phenol
   (d) None of these.

5. The solubility of $BaSO_4$ in water is 2.33×10^{-3} g/L. Its solubility product will be (molecular weight of $BaSO_4 = 233$)
   (a) 1×10^{-15} (b) 1×10^{-10}
   (c) 1×10^{-5} (d) 1×10^{-20}

6. Which of the following is a heterocyclic compound?
   (a) Furan   (b) Pyridine
   (c) Thiophene   (d) All are correct.

7. In which of the following reactions methane is formed?

   (a) $CH_3COOH \xrightarrow{[H]}$
   (b) $CH_3COOH \xrightarrow{NaOH/CaO}$
   (c) $CH_3COOH \xrightarrow{[O]}$
   (d) $CH_3CH_2COOH \xrightarrow{NaOH/CaO}$

8. Which of the following alkaline earth metals has highest ionic mobility in aqueous solution?
   (a) Be^{2+} (b) Ca^{2+}
   (c) Ba^{2+} (d) Mg^{2+}

9. Which of the following is formed, when benzaldehyde reacts with alcoholic KCN?
   (a) Benzoin   (b) Benzyl alcohol
   (c) Benzoic acid   (d) Ethyl benzoate

10. Coefficients p, q and r in the following reaction $pFeCr_2O_4 + qNaOH + rO_2 \rightarrow Na_2CrO_4 + Fe_2O_3 + H_2O$ are
    (a) 5, 10, 5   (b) 3, 5, 6
    (c) 4, 16, 7   (d) 4, 14, 9

11. An element (atomic mass 100 g/mol) having bcc structure has unit cell edge 400 pm. The density of element is [No. of atoms in bcc (Z) = 2]
    (a) 2.144 g/cm³   (b) 7.289 g/cm³
    (c) 5.188 g/cm³   (d) 10.376 g/cm³

12. Ozonolysis product of cyclobutene is
    (a) glyoxal   (b) dimethylglyoxal
    (c) succinaldehyde   (d) methanal.

13. A first order reaction, which is 30% complete in 30 minutes has a half-life period of
    (a) 102.2 min   (b) 58.2 min
    (c) 24.2 min   (d) 120.2 min

14. Permanent hardness of water can be removed by adding
    (a) Na_2CO_3 (b) K
    (c) $Ca(OCl)Cl$ (d) Cl_2

15. The major product of the reaction between m-dinitrobenzene with NH_4HS is

(a)

(b)

(c)

(d)
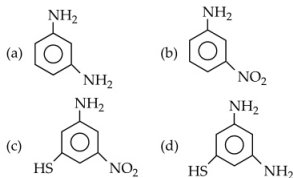
16. A certain aqueous solution of $FeCl_3$ [formula mass = 162] has a density of 1.1 g/mL and contains 20.0% $FeCl_3$. Molar concentration of this solution is
(a) 0.028 M
(b) 0.163 M
(c) 1.357 M
(d) 1.47 M

17. Hydrolysis of 1,1-dichloroethane with aqueous potassium hydroxide gives
(a) ethene
(b) ethyne
(c) ethylene glycol
(d) ethanal.

18. Which of the following reactions will yield 2-propanol?

I. $CH_2=CH-CH_3 + H_2O \xrightarrow{H^+}$

II. $CH_3-CHO \xrightarrow{\text{(i) } CH_3MgI} \xrightarrow{\text{(ii) } H_2O}$

III. $CH_2O \xrightarrow{\text{(i) } C_2H_5MgI} \xrightarrow{\text{(ii) } H_2O}$

IV. $CH_2=CH-CH_3 \xrightarrow{\text{Neutral } KMnO_4}$
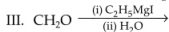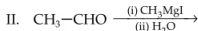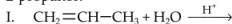
(a) I and II
(b) II and III
(c) III and I
(d) II and IV

19. A particular reaction has a negative value for the free energy change. Then at ordinary temperature,
(a) it has a large –ve value for the entropy change
(b) it has a large +ve value for the enthalpy change
(c) it has a small +ve value for enthalpy change
(d) it has a +ve value for the entropy change and a –ve value for the enthalpy change.

20. Glucose $\xrightarrow{HCN} \xrightarrow{Hydrolysis} \xrightarrow{HI, heat} A$, A is
(a) heptanoic acid
(b) 2-iodohexane
(c) heptane
(d) heptanol.

21. Ionization potential of hydrogen atom is 13.6 eV. Hydrogen atom in ground state is excited by monochromatic light of energy 12.1 eV. The spectral lines emitted by hydrogen according to Bohr's theory will be
(a) one
(b) two
(c) three
(d) four.

22. Which of the following order about their basic strengths is correct?
(a) $NH_3 < NH_2OH < HN_3 < NH_2NH_2$
(b) $NH_2OH < HN_3 < NH_2NH_2 < NH_3$
(c) $HN_3 < NH_3 < NH_2OH < NH_2NH_2$
(d) $HN_3 < NH_2OH < NH_2NH_2 < NH_3$

23. Amongst the acids,
(i) $CH\equiv CCOOH$
(ii) $CH_2=CHCOOH$ and
(iii) CH_3CH_2COOH,
the acid strength follows the sequence
(a) (i) < (ii) > (iii)
(b) (i) > (ii) > (iii)
(c) (i) = (ii) = (iii)
(d) (i) = (ii) > (iii)

24. Which of the following statement is true for an electrochemical cell?
(a) H_2 is anode and Cu is cathode
(b) H_2 is cathode and Cu is anode
(c) reduction occurs at H_2 electrode
(d) oxidation occurs at Cu electrode

25. If 0.189 g of a chlorine containing organic compound gives 0.287 g of silver chloride, then the percentage of chlorine in the organic compound is
(a) 35.47
(b) 35.57
(c) 37.57
(d) 45.37

26. Gold number of few colloids are given below :
Gelatin = 0.005   Starch = 25
Egg albumin = 0.18   Gum arabic = 0.23
Which is best protective colloid?
(a) Gelatin
(b) Starch
(c) Egg albumin
(d) Gum arabic

27. Arsenic drugs are mainly used in the treatment of
(a) Jaundice
(b) Typhoid
(c) Syphilis
(d) Cholera.

28. Oxygen is not evolved when conc. H_2SO_4 reacts with
(a) $KMnO_4$
(b) MnO_2
(c) $K_2Cr_2O_7$
(d) $CuSO_4$

29. Electron is an alloy of
(a) Ni and Zn
(b) Fe and Mg
(c) Mg and Zn
(d) Al and Zn

30. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25°C and it increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at 25°C is 0.998 cal/g-deg, the value of the heat of combustion of benzoic acid is
(a) 881.1 kcal
(b) 771.12 kcal
(c) 981.1 kcal
(d) 871.2 kcal

31. Which of the following on reaction with nitrous acid followed by treatment with NaOH produces a blue colouration ?
(a) RCH_2NO_2
(b) R_3CNO_2
(c) $C_6H_5NO_2$
(d) R_2CHNO_2

32. Which of the following combinations illustrates the law of reciprocal proportions?
(a) N_2O_3, N_2O_4, N_2O_5
(b) NaCl, NaBr, NaI
(c) CS_2, CO_2, SO_2
(d) PH_3, P_2O_3, P_2O_5

33. Which of the following is the correct order of stability of the following four distinct conformation of n-butane?

(a) Staggered > Gauche > Partially eclipsed > Fully eclipsed

(b) Gauche > Staggered > Partially eclipsed > Fully eclipsed

(c) Staggered > Partially eclipsed > Gauche > Fully eclipsed

(d) Fully eclipsed > Staggered > Partially eclipsed > Gauche

34. $CuSO_4$ reacts with KCN solution and forms
    (a) $K_3[Cu(CN)_4]$ (b) CuCN
    (c) $Cu[Cu(CN)_2]$ (d) $K_4[Cu(CN)_6]$

35. The correct order of solubility of fluorides of alkaline earth metals is
    (a) $MgF_2 > BaF_2 > SrF_2 > CaF_2 > BeF_2$
    (b) $BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2$
    (c) $BeF_2 > BaF_2 > SrF_2 > CaF_2 > MgF_2$
    (d) None of these.

36. Two elements A and B form compounds of formula AB_2 and AB_4. When dissolved in 20.0 g of benzene 1.0 g of AB_2 lowers f. pt. by 2.3°C whereas 1.0 g of AB_4 lowers f. pt. by 1.3°C. The K_f for benzene is 5.1. The atomic masses of A and B are
    (a) 25, 42   (b) 42, 25   (c) 52, 48   (d) 48, 52

37. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couple.
$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$
What will be the equilibrium constant for the reaction?
    (a) 7.07×10^8 (b) 7.07×10^3
    (c) 6.07×10^9 (d) 6.07×10^7

38. The true statement for the acids of phosphorus, H_3PO_2, H_3PO_3 and H_3PO_4 is
    (a) the order of their acidity is $H_3PO_4 > H_3PO_3 > H_3PO_2$
    (b) all of them are reducing in nature
    (c) all of them are tribasic acids
    (d) the geometry of phosphorus is tetrahedral in all the three.

39. The colourless species is
    (a) VCl_3 (b) $VOSO_4$
    (c) Na_3VO_4 (d) $[V(H_2O)_6]SO_4 \cdot H_2O$

40. A hydride of nitrogen which is acidic is
    (a) NH_3 (b) N_2H_4
    (c) N_2H_2 (d) N_3H

ASSERTION AND REASON

Directions : In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

41. **Assertion :** The dimerization reaction of NO_2 gas to N_2O_4 is an exothermic reaction.
$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}; \Delta H = -57.2 \text{ kJ mol}^{-1}$$
Reason : Increase in temperature shifts the equilibrium in the forward direction.
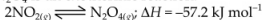
42. **Assertion :** Cyclobutane is less stable than cyclopentane.
Reason : In cycloalkanes, as the ring size increases angle strain decreases.

43. **Assertion :** PbO_2 is a powerful oxidising agent, it evolves O_2 gas on reaction with conc. H_2SO_4.
Reason : Due to inert pair effect, +2 oxidation state of Pb is the most stable.

44. **Assertion :** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction occurs by S_N1 mechanism.

45. **Assertion :** N_2 and NO^+ both are diamagnetic.
Reason : NO^+ is isoelectronic with N_2.

46. **Assertion :** Benzaldehyde is less reactive than ethanal towards nucleophilic attack.
Reason : The overall effect of $-I$ and $+R$ effect of phenyl group decreases the electron density on the carbon atom of $\rangle C=O$ group in benzaldehyde.

47. **Assertion :** The total number of isomers shown by $[Co(en)_2Cl_2]^+$ complex ion is three.
Reason : $[Co(en)_2Cl_2]^+$ complex ion has an octahedral geometry.

48. **Assertion :** Bond order in a molecule, can assume any value positive or negative, integral or fractional including zero.
Reason : Bond order depends on the number of electrons in the bonding and antibonding orbitals.

49. **Assertion :** Nitrobenzene undergoes electrophilic substitution at m-position while nucleophilic substitution occurs at o- and p-positions.
Reason : Nitro group in benzene ring significantly lowers the electron density at o- and p-positions while at m-position, the electron density is only originally lowered.

50. **Assertion :** The ease of dehydration of alcohols follows the order :
Tertiary > Secondary > Primary
Reason : Dehydration proceeds through the formation of oxonium ions.

51. **Assertion :** The second ionization energies of $_{23}V$, $_{24}Cr$ and $_{25}Mn$ are in the order V < Cr < Mn.
Reason : Ionization energies show a regular increase along a period with increase of atomic number.
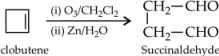
52. Assertion : 0.003500 has six significant figures.
Reason : Zeros to the left of the first non-zero digit in a number are signifcant.
But if a number ends in zeros and these zeros are to the right of the decimal point, then these zeros are not significant.

53. Assertion : Pure acetic acid is converted into ice like solid called glacial acetic acid.
Reason : Acetic acid is stronger than formic acid.

54. Assertion : Conductivity of silicon increases by doping it with group-15 elements.
Reason : Doping means introduction of small amount of impurities like P, As or Bi into the pure crystal.

55. Assertion : Ionization potential across the period is Na < Al < Mg < Si.
Reason : Ionization potential decreases with decrease in atomic size.

56. Assertion : Benzene reacts with n-propyl chloride in presence of $AlCl_3$ to give isopropyl benzene.
Reason : Benzene undergoes electrophilic substitution readily.

57. Assertion : If standard reduction potential for the reaction $Ag^+ + e^- \rightarrow Ag$ is 0.80 volt, then for the reaction $2Ag^+ + 2e^- \rightarrow 2Ag$, it will be 1.60 volt.
Reason : If concentration of Ag^+ ions is doubled, its standard electrode potential is also doubled.

58. Assertion : Both chlorine and sulphur dioxide act as bleaching agents.
Reason : Chlorine bleaches by mild reduction, while sulphur dioxide bleaches by vigorous oxidation.

59. Assertion : If 100 cc of 0.1 N HCl is mixed with 100 cc of 0.2 N HCl, the normality of the final solution will be 0.30.
Reason : Normalities of similar solutions like HCl can be added.

60. Assertion : $BeSO_4$ is soluble in water while $BaSO_4$ is not.
Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant.

<table>
<tr><td colspan="4" align="center">**SOLUTIONS**</td></tr>
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1. (b) :
SF_6	sp^3d^2	Octahedral
IF_7	sp^3d^3	Pentagonal bipyramidal
PF_5	sp^3d	Trigonal bipyramidal
$SnCl_4$	sp^3	Tetrahedral

2. (d) : $T_1 > T_2$
$\upsilon_1 > \upsilon_2$
$f_2 > f_1$

3. (b) : In EDTA, donor atoms are two N and four O.

4. (b) : Since a stronger acid displaces a weaker acid from its salts, therefore, carbonic acid ($CO_2 + H_2O$ $\equiv H_2CO_3$) is a stronger acid than phenol.

5. (b) : Solubility of $BaSO_4$ in $gL^{-1} = 2.33 \times 10^{-3}$
Solubility of $BaSO_4$ in mol $L^{-1} = \dfrac{2.33}{233} \times 10^{-3} = 10^{-5}$
Now, $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$
Solubility s s
$\therefore$ Solubility Product $= [Ba^{2+}][SO_4^{2-}] = s^2$
$= (10^{-5})^2 = 10^{-10}$

6. (d) :

Furan   Pyridine   Thiophene

7. (b) : $CH_3COOH \xrightarrow{NaOH/CaO} CH_4 + Na_2CO_3$
When sodium salt of carboxylic acid is heated with soda lime (NaOH + CaO), alkane is obtained with one less carbon atom than the parent acid, and the process is called decarboxylation.

8. (c) : Due to high heat of hydration of small cations, ionic mobility for the small cations is low. Order of ionic mobility is :
$Be^{2+} < Mg^{2+} < Ca^{2+} < Ba^{2+}$

9. (a) : $2C_6H_5CHO \xrightarrow[\Delta]{alc. KCN} C_6H_5CH(OH)COC_6H_5$
      Benzaldehyde   Benzoin
The reaction is known as benzoin condensation.

10. (c) : $4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4$
$+ 2Fe_2O_3 + 8H_2O$

11. (c) : If edge length of the cube is in pm then density,
$\rho = \dfrac{Z \times M}{a^3 \times N_0 \times 10^{-30}}$ g cm^{-3}
$\therefore$ $\rho = \dfrac{2 \times 100}{(400)^3 \times 6.023 \times 10^{23} \times 10^{-30}} = 5.188$ g/cm^3

12. (c) :

Cyclobutene   Succinaldehyde

13. (b) : For first order reaction,
$t = \dfrac{2.303}{k} \log \dfrac{a}{a-x} \Rightarrow \dfrac{t_{30\%}}{t_{50\%}} = \dfrac{\dfrac{2.303}{k} \log \dfrac{100}{100-30}}{\dfrac{2.303}{k} \log \dfrac{100}{100-50}}$

$$\Rightarrow \frac{30}{t_{1/2}} = \frac{\log \frac{10}{7}}{\log 2} \Rightarrow \frac{30}{t_{1/2}} = \frac{0.1549}{0.3010}$$

$$\Rightarrow t_{1/2} = \frac{0.3010 \times 30}{0.1549} = 58.29 \text{ min}$$

14. (a) : When hard water is treated with a certain amount of washing soda (Na_2CO_3), the chlorides and sulphates of calcium and magnesium are converted into their respective carbonates, which get precipitated. As a result of this, the hardness of water can be removed.

15. (b) :

m-Dinitrobenzene → m-Nitroaniline (Major product)

with NH_4HS, Δ
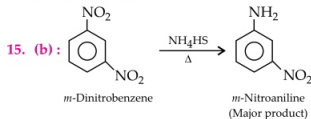
16. (c) : 20% $FeCl_3$ solution means 100 g of solution contains 20 g of $FeCl_3$.

$$\therefore \quad \text{Volume of 100 g solution} = \frac{100 \text{ g}}{1.1 \text{ g/mL}}$$

$$= 90.91 \text{ mL}$$

$$\text{Moles of 20 g of } FeCl_3 = \frac{20}{162} = 0.1234 \text{ mole}$$

$\therefore$ Molar concentration of solution

$$= \frac{0.1234}{90.91} \times 1000 = 1.357 \text{ M}$$

17. (d) :

$$CH_3CHCl_2 + 2KOH_{(aq.)} \longrightarrow CH_3CH(OH)_2$$

1,1-Dichloroethane   Unstable

$$\downarrow$$

$$CH_3CHO$$

Ethanal

18. (a) : I. $CH_3CH{=}CH_2 + H_2O \xrightarrow{H^+} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

2-Propanol

II. $CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

2-Propanol

III. $CH_2O \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgI} C_2H_5CH_2OH$

1-Propanol

IV. $CH_3CH{=}CH_2 \xrightarrow[\text{neutral}]{KMnO_4} CH_3\overset{\overset{\displaystyle |}{C}H}{\underset{\underset{\displaystyle OH}{|}}{}}CH_2\text{(with HO)}$

Propan-1,2-diol
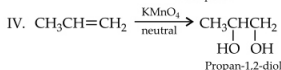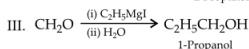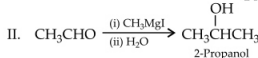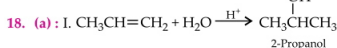
19. (d) : $\Delta G = \Delta H - T\Delta S$ can be negative at ordinary T if ΔH is −ve and ΔS is +ve.

20. (a) :

Glucose $\xrightarrow{HCN}$ Glucose cyanohydrin $\xrightarrow{\text{Hydrolysis}}$

$CH_3(CH_2)_5COOH \xleftarrow{HI/heat}$
Heptanoic acid
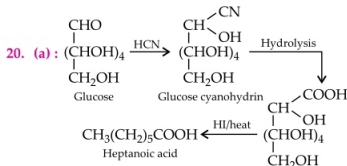
21. (c) : Since ionization potential of hydrogen atom is 13.6 eV.

$\therefore \quad E_1 = -13.6 \text{ eV}$

Now, $E_n - E_1 = \frac{-13.6}{n^2} - (-13.6) = 12.1$

$$\frac{-13.6}{n^2} + 13.6 = 12.1$$

$\therefore \quad n = 3$

After absorbing 12.1 eV the electron in H atom is excited to 3rd shell.

Thus, possible transitions are 3
i.e., $3 \rightarrow 2$, $2 \rightarrow 1$ and $3 \rightarrow 1$.

22. (b) : Basicity in nitrogen compounds is attributed to the availability of lone pair of electrons.
Putting more electronegative groups on N will decrease its basicity.
Therefore, the order of basicity of these compounds is :

$$NH_3 > NH_2NH_2 > HN_3 > NH_2OH.$$
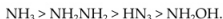
23. (b) : Since sp-hybridized carbon is more electronegative than a sp^2-hybridized carbon which in turn is more electronegative than sp^3-hybridized carbon, therefore, $\underset{sp}{CH{\equiv}C}{-}COOH$ is a stronger acid than $\underset{sp^2}{CH_2{=}CH}{-}COOH$ which in turn, is a stronger acid than $\underset{sp^3}{CH_3{-}CH_2}{-}COOH$. Thus, the overall order of acid strength is (i) > (ii) > (iii).

24. (a) : As Cu is below hydrogen in the Electrochemical series. Hydrogen is oxidised at anode and comes out as H_2 while Cu is reduced at the cathode.
$2H^+ + 2e^- \rightarrow H_2$, $E° = 0.0$ volt
$Cu^{2+} + 2e^- \rightarrow Cu$, $E° = 0.337$ volt
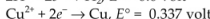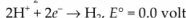
25. (c) : According to Carius method,
% of chlorine in organic compound

$$= \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed} \times 100}{\text{Mass of substance taken}}$$

$$= \frac{35.5 \times 0.287}{143.5 \times 0.189} \times 100 = 37.57\%$$

26. (a) : Lesser is gold number, more is the protective power of lyophilic colloid.

27. (c) : Arsenic drugs such as salvarsan is used for treatment of syphilis.

28. (d) : $CuSO_4$ does not react with H_2SO_4. All other compounds give O_2 on reacting with conc. H_2SO_4.

29. (c) : A typical electron alloy has the composition : Mg(95%), Cu(4.5%), Zn(0.5%)

30. (b) : Given : Weight of benzoic acid = 1.89 g; Temperature of bomb calorimeter = 25°C = 298 K; Mass of water (m) = 18.94 kg = 18940 g; Increase in temperature (t) = 0.632°C and specific heat of water (s) = 0.998 cal/g-deg.
We know that heat gained by water or heat liberated by benzoic acid (Q) = $ms\Delta t$
= 18940 × 0.998 × 0.632 = 11946.14 cal
Since 1.89 g of acid liberates 11946.14 cal of heat, therefore heat liberated by 122 g (mol. wt. of benzoic acid) of acid
$$= \frac{11946.14 \times 122}{1.89} = 771126.5 \text{ cal} = 771.12 \text{ kcal}$$

31. (d) : 2° nitroalkanes react with HNO_2 to give pseudo nitroles which on treatment with NaOH produces blue colouration.

32. (c) : In law of reciprocal proportions, the two elements combining with the third element, must combine with each other in the same ratio or multiple of that ratio. Ratio of S and O when combine with C is 2 : 1. Ratio of S and O in SO_2 is 1 : 1. Thus, the two ratios are simple multiple of each other.

33. (a) : Staggered > Gauche > Partially eclipsed > Fully eclipsed

34. (a) : When potassium cyanide is added to a solution of copper sulphate, CN^- ions first reduce Cu^{2+} to Cu^+ which then combines with CN^- ions to form insoluble cuprous cyanide which subsequently dissolves in excess of KCN to give the complex compound, potassium tetracyanocuprate(I)

$2Cu^{2+} + 2CN^- \longrightarrow 2Cu^+ + \underset{\text{Cyanogen}}{(CN)_2}$

$Cu^+ + CN^- \longrightarrow CuCN \downarrow$

$CuCN + 3KCN \longrightarrow \underset{\substack{\text{Pot. tetracyanocuprate(I)}\\ \text{(Soluble complex)}}}{K_3[Cu(CN)_4]}$

35. (c) : BeF_2 is highly soluble in water due to the high hydration energy of the small Be^{2+} ion. The other fluorides (MgF_2, CaF_2, SrF_2 and BaF_2) are almost insoluble in water. Since on descending the group lattice energy decreases more rapidly than the hydration energy. Therefore, whatever little solubility these fluorides have that increases down the group.

36. (a) : Let the masses of A and B be a and b. The mass of AB_2 will be ($a + 2b$) g mol^{-1} and AB_4 will be ($a + 4b$) g mol^{-1}.

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

For AB_2, $2.3 = \dfrac{5.1 \times 1 \times 1000}{(a + 2b) \times 20}$ ...(i)

For AB_4, $1.3 = \dfrac{5.1 \times 1 \times 1000}{(a + 4b) \times 20}$ ...(ii)

On solving (i) and (ii), we get
$a = 25.59$ and $b = 42.64$

37. (d) : $E^{\circ}_{cell} = E_{cathode} - E_{anode}$
= 0.77 − 0.54 = 0.23 V

$\Delta G = -nFE^{\circ}_{cell} = -RT \ln K$ or $E^{\circ}_{cell} = \dfrac{0.0591}{n} \log K$

$\log K = \dfrac{0.23 \times 2}{0.0591} = 7.783$

or K = Antilog (7.783) = 6.07×10^7

38. (d) : There is very little difference in their acidity.
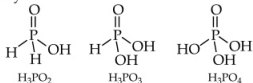
H_3PO_2 H_3PO_3 H_3PO_4

Reducing nature depends on no. of P—H bonds. More the no. of P—H bonds, more will be the reducing nature. Thus, H_3PO_2 is stronger reducing agent than H_3PO_3 while H_3PO_4 does not act as reducing agent at all.
H_3PO_2, H_3PO_3 and H_3PO_4 contain one, two and three ionisable hydrogen atoms (P—OH bonds) respectively.
As sp^3 hybridised, therefore all are tetrahedral.

39. (c) : Na_3VO_4 contains colourless vanadate (VO_4^{3-}) ion. Oxidation state of V in VO_4^{3-} ion is +5.
V^{5+} : $3d^0 4s^0$, does not have unpaired electron hence d-d transition is not possible.

40. (d) : N_3H (hydrazoic acid) is the acidic hydride of nitrogen.

41. (c) : Since the reaction is exothermic, therefore increase in temperature shifts the equilibrium in the backward direction, whereas decrease in temperature favours the reaction in forward direction.

42. (a) : Cyclopentane is more stable because it can relieve some of the bond strain by buckling the ring and pushing one carbon out of the plane. Cyclobutane is highly strained.

43. (a)

44. (a) : In S_N1 mechanism, racemization takes place due to the reason, that planar carbocations are the intermediates and hence attack of nucleophile can take place from both the sides.

45. (b) : Due to the absence of unpaired electron in NO^+ and N_2, both are diamagnetic.

$$[:N \equiv \overset{..}{O}:]^+; \; :N \equiv N:$$

total no. of e^- in $NO^+ = 7 + 8 - 1 = 14$
total no. of e^- in $N_2 = 7 + 7 = 14$
Therefore, both are isoelectronic.

46. (c) : Benzaldehyde is less reactive than ethanal towards nucleophilic attack. The combined effect of $-I$ and $+R$ effects of phenyl group is electron donating which increases the electron density on the carbon atom of the $>C=O$ in benzaldehyde, thereby repelling the nucleophiles.

47. (b) : $[Co(en)_2Cl_2]^+$ exist in *cis* and *trans* isomers out of which *cis* isomer will be optically active (*cis-d*-isomer) and (*cis-l*-isomer).

48. (a) : Bond order is the half of the difference between bonding and anti-bonding electrons.
Bond order

$$= \frac{1}{2}\left[\left(\begin{array}{c} \text{no. of } e^- \text{ in} \\ \text{bonding M.O.} \end{array}\right) - \left(\begin{array}{c} \text{no. of } e^- \text{ in} \\ \text{antibonding M.O.} \end{array}\right)\right]$$

Higher the value of bond order, stronger is the bond.

49. (a) : $-NO_2$ group withdraws electrons from *o*- and *p*-positions. Thus, *m*-position becomes a point of relatively high electron density and further substitution by electrophile occurs at *m*-position.

50. (b) : In dehydration of alcohols leading to formation of alkenes, carbocation is formed in rate determining step.
The order of stability of carbocations is $3° > 2° > 1°$. Therefore, ease of dehydration follows the same order.
Oxonium ions (protonated alcohol molecule) are formed in the first step of reaction mechanism.

51. (d) : The correct order of 2nd IE is $_{23}V < _{24}Cr > _{25}Mn$. Cr has losing one electron has $3d^5$ half filled stable configuration from which removal of second electron is difficult.

52. (d) : Zeros to the left of the first non-zero digit in a number are not significant.
If a number ends in zeros but these zeros are to the right of the decimal point, then these zero are significant.
Hence, 0.003500 has four significant figures.

53. (c) : Formic acid is stronger than acetic acid. $+I$ effect of $-CH_3$ group will increase the electron density in $O-H$ bond and thus release of H^+ ion will be more difficult in acetic acid as compared to formic acid. Further, $+I$ effect of $-CH_3$ group also destabilizes the acetate ion relative to the formate ion by intensifying the $-ve$ charge on carboxylate ion.

54. (b) : When a silicon crystal is doped with a group-15 element like P, As, Sb or Bi, the silicon atoms at some lattice sites are substituted by atoms of group-15 element. As these atoms have 5 electrons in the valence shell, after forming normal four covalent bonds with silicon atom, the fifth extra electron is free and gets delocalized and hence increases the conductivity of silicon.

55. (c) : Ionization potential decreases with increase in atomic size and also for a given shell, *I.E.* is in given order $s > p > d > f$.

56. (b) : When Friedel–Craft alkylation is carried out with $CH_3CH_2CH_2Cl$, the product obtained is isopropyl benzene because the initially formed *n*-propyl carbocation being less stable first rearranges to the more stable isopropyl carbocation by 1,2-hydride shift before attacking the benzene ring.

$$CH_3 - \underset{\underset{\text{H}}{|}}{CH} - \overset{+}{CH_2} \longrightarrow CH_3 - \overset{+}{CH} - CH_3$$

(1° carbocation)   (2° carbocation)

57. (d) : Standard reduction potential of an electrode has a fixed value. Effect of concentration is studied by Nernst equation.

58. (c) : SO_2 in presence of moisture acts as a mild bleaching agent. This is due to the reducing nature of SO_2. But bleaching action is only temporary.
$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$$
Similarly, Cl_2 in presence of moisture gives out nascent oxygen and hence causes bleaching due to oxidation.
$$Cl_2 + H_2O \rightarrow 2HCl + [O]$$
here bleaching action is permanent.

59. (d) : If 100 cc of 0.1 N HCl is mixed with 100 cc of 0.2 N HCl, the normality of the final solution will be 0.15.
$$N_1V_1 + N_2V_2 = N_3V_3$$
i.e., $0.1 \times 100 + 0.2 \times 100 = N_3 \times 200$
or $N_3 = \dfrac{0.3 \times 100}{200} = 0.15$ N

60. (a)

■■

NCER CORNER

CLASS XI-XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry. Last year JEE (Main & Advanced) / NEET / AIIMS / other PMTs have drawn their papers heavily from NCERT books. Practise hard ! All the best !!

1. The SI unit of viscosity coefficient is
   (a) pascal
   (b) poise
   (c) decapoise
   (d) newton.

2. Which of the following unit cells is most unsymmetrical?
   (a) Triclinic
   (b) Orthorhombic
   (c) Monoclinic
   (d) Hexagonal

3. In the organic compound
   $CH \equiv C — CH_2 — CH = CH_2$, the pair of hybridised orbitals involved in the formation of $C_2 — C_3$ bond is
   (a) $sp – sp$
   (b) $sp^3 – sp^2$
   (c) $sp – sp^3$
   (d) $sp^2 – sp^3$

4. Amongst the following, the most stable complex is
   (a) $[Fe(H_2O)_6]^{3+}$
   (b) $[Fe(NH_3)_6]^{3+}$
   (c) $[Fe(C_2O_4)_3]^{3-}$
   (d) $[FeCl_6]^{3-}$

5. If the density of a solution is $3.12\ g\ mL^{-1}$, the mass of 1.5 mL solution in significant figures is
   (a) 4.7 g
   (b) 4680×10^{-3} g
   (c) 4.680 g
   (d) 46.80 g

6. Identify the correct statement.
   (a) *p*-Toluidine is less basic than *m*-toluidine.
   (b) *o*-Toluidine is more basic than aniline.
   (c) *o*-Toluidine is more basic than *p*-toluidine.
   (d) *m*-Toluidine is more basic than aniline.

7. Which of the following arrangements represent increasing oxidation number of the central atom?
   (a) $CrO_2, ClO_3^-, CrO_4^{2-}, MnO_4^-$,
   (b) $ClO_3^-, CrO_4^{2-}, MnO_4^-, CrO_2$,
   (c) $CrO_2, ClO_3^-, MnO_4^-, CrO_4^{2-}$
   (d) $CrO_4^{2-}, MnO_4^-, CrO_2, ClO_3^-$

8. Molar conductivities for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 S cm^2 mol^{-1} respectively. The molar conductivity for NH_4OH is (in S cm^2 mol^{-1})
   (a) 523.28
   (b) 251.44
   (c) 428.54
   (d) 308.71

9. On ozonolysis 4, 5-diethylcyclohexene gives
   (a) only a ketone
   (b) an aldehdye and a ketone
   (c) only an aldehyde
   (d) a dialdehyde.

10. When the concentration is expressed as the number of moles of a solute per kilogram of the solvent, it is known as
    (a) molarity
    (b) molality
    (c) normality
    (d) mole fraction.

11. Four electrons, identified by quantum numbers n and l (i) $n = 4, l = 1$; (ii) $n = 4, l = 0$; (iii) $n = 3, l = 2$; (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as
    (a) (iv) < (ii) < (iii) < (i)
    (b) (ii) < (iv) < (i) < (iii)
    (c) (i) < (iii) < (ii) < (iv)
    (d) (iii) < (i) < (iv) < (ii)

12. Shape and hybridisation of P in PCl_5 molecule is
    (a) trigonal bipyramidal, dsp^3
    (b) trigonal bipyramidal, sp^3d
    (c) square pyramidal, sp^3d^2
    (d) T-shaped, sp^3d

13. Which is not a pyrimidine base?
    (a) Uracil
    (b) Thymine
    (c) Cytosine
    (d) Guanine

14. Favourable conditions for the formation of $NH_{3(g)}$ in good yield by using
    $$N_{2(g)} + 3H_{2(g)} – 22\ kcal \rightleftharpoons 2NH_{3(g)}$$
    are
    (a) high T and high P
    (b) high T and low P
    (c) low T and high P
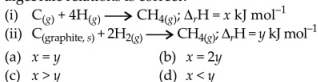   (d) high T, low P and presence of a catalyst.

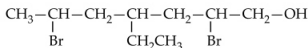15. Consider the figure below and mark the correct option.
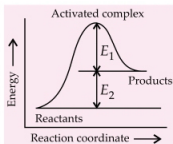
(a) Activation energy of forward reaction is $E_1 + E_2$ and products are less stable than reactants.

(b) Activation energy of forward reaction is $E_1 + E_2$ and products are more stable than reactants.

(c) Activation energy of both forward and backward reactions is $E_1 + E_2$ and reactants are more stable than products.

(d) Activation energy of backward reaction is E_1 and products are more stable than reactants.

16. Aldol condensation will not occur in
   (a) HCHO   (b) CH_3CH_2CHO
   (c) CH_3COCH_3 (d) CH_3CHO

17. Boron trifluoride on treatment with lithium aluminium hydride in diethyl ether gives
   (a) boric acid   (b) borazine
   (c) diborane   (d) borax.

18. Barbituric acid and its derivatives are well known
   (a) analgesics   (b) antipyretics
   (c) tranquilizers   (d) antiseptics.

19. Which of the following compounds is used for water softening?
   (a) $Ca_3(PO_4)_2$ (b) Na_3PO_4
   (c) $Na_6P_6O_{18}$ (d) Na_2HPO_4

20. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
   (a) CO
   (b) Hydrocarbon
   (c) Peroxyacetyl nitrate
   (d) NO

21. The atomic numbers of other elements which lie in the same group as the tenth element in the periodic table are
   (a) 18, 32, 54, 86   (b) 8, 18, 36, 84
   (c) 2, 18, 30, 36   (d) 2, 18, 36, 54

22. Which of the following is the example of addition copolymer?
   (a) Buna-S   (b) Nylon-2, 6
   (c) Alkyd resin   (d) PTFE

23. Consider the reactions given below. On the basis of these reactions find out which of the following algebraic relations is correct?
   (i) $C_{(g)} + 4H_{(g)} \longrightarrow CH_{4(g)};\ \Delta_r H = x\ kJ\ mol^{-1}$
   (ii) $C_{(graphite,\ s)} + 2H_{2(g)} \longrightarrow CH_{4(g)};\ \Delta_r H = y\ kJ\ mol^{-1}$
   (a) $x = y$ (b) $x = 2y$
   (c) $x > y$ (d) $x < y$

24. The IUPAC name of the following compound is

$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{Br}{|}}{CH}-CH_2-OH$$

   (a) 2, 6-dibromo-4-ethylheptan-1-ol
   (b) 2, 6-dibromo-4-ethylheptan-7-ol
   (c) 1-hydroxy-2, 6-dibromo-4-ethylheptane
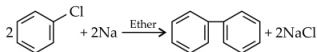   (d) 4-ethyl-2, 6-dibromoheptan-1-ol.

25. Compound of xenon which is isostructural with IBr_2^- is
   (a) XeO_3 (b) XeF_2
   (c) XeF_4 (d) $XeOF_4$

26. Among the following metal halides of group 2, the one which is soluble in ethanol is
   (a) $BeCl_2$ (b) $MgCl_2$
   (c) $CaCl_2$ (d) $SrCl_2$

27. Following reaction is an example of

   (a) Wurtz-Fittig reaction
   (b) Fittig reaction
   (c) Wurtz reaction
   (d) Kolbe's reaction.

28. Which of the following is incorrect statement?
   (a) For physisorption, low temperature is favourable.
   (b) Physisorption is not specific in nature.
   (c) Physisorption is irreversible in nature.
   (d) For chemisorption, high temperature is favourable.

29. Which of the following ions are colourless?
   $$Ti^{3+},\quad Sc^{3+},\quad Ag^+,\quad Cd^{2+},\quad Cu^{2+}$$
   $$\ \ I\qquad\ \ II\qquad\ III\qquad\ IV\qquad\ V$$
   (a) I and V only   (b) II, III and IV only
   (c) I, III and V only   (d) III and IV only

30. Which of the following metals is obtained by electrolytic reduction process?
    (a) Fe
    (b) Cu
    (c) Ag
    (d) Al

31. Identify the correct statement.
    (a) Stability of the molecule is directly proportional to the number of antibonding electrons.
    (b) Bond length is inversely proportional to the bond order.
    (c) Bond dissociation energy is directly proportional to the bond order.
    (d) Both (b) and (c).

32. Hydrolysis of optically active 2-bromobutane results in the formation of
    (a) (+)-butan-2-ol
    (b) (–)-butan-2-ol
    (c) (±)-butan-2-ol
    (d) but-1-ene.

33. pH of 0.01 M $(NH_4)_2SO_4$ and 0.02 M NH_4OH buffer (pK_a of NH_4^+ = 9.26) is
    (a) 4.74 + log 2
    (b) 4.74 – log 2
    (c) 4.74 + log 1
    (d) 9.26 + log 1

34. The final product of the following reaction is
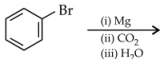
    (a) benzaldehyde
    (b) benzene
    (c) benzoic acid
    (d) phenol.

35. The rate constant of nth order reaction has units
    (a) $L^{1-n} mol^{n-1} s^{-1}$
    (b) $mol^{1-n} L^{1-n} s^{-1}$
    (c) $mol^{1-n} L^{n-1} s^{-1}$
    (d) none of these.

36. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with
    (a) methyl bromide
    (b) ethyl iodide and magnesium
    (c) methyl iodide and magnesium
    (d) methyl bromide and aluminium bromide.

37. In acidic solution, MnO_4^- is
    (a) oxidised by 3 electrons
    (b) reduced by 3 electrons
    (c) oxidised by 5 electrons
    (d) reduced by 5 electrons.

38. One of the monomers of dacron is
    (a) acrylonitrile
    (b) formaldehyde
    (c) ethylene glycol
    (d) phthalic acid.

39. Number of σ and π bonds in benzophenone is
    (a) 24, 6
    (b) 25, 6
    (c) 25, 7
    (d) 24, 7

40. Which of the following amides will not undergo Hofmann bromamide reaction?
    (a) CH_3CONH_2
    (b) $CH_3CH_2CONH_2$
    (c) $C_6H_5CONH_2$
    (d) $CH_3CONHCH_3$

41. How many significant figures are present in 0.0000135?
    (a) 7
    (b) 8
    (c) 4
    (d) 3

42. Carbon atom in methyl carbocation and methyl carbanion is ____ and ____ hybridised.
    (a) sp^3, sp^2
    (b) sp^2, sp^3
    (c) sp, sp^2
    (d) sp^3, sp

43. Chemical formula of tear gas is
    (a) CCl_3NH_2
    (b) CCl_3NO_2
    (c) CH_2Cl_2
    (d) $COCl_2$

44. Correct name of the following complex is $[Cr(H_2O)_4Cl_2]NO_3$
    (a) dichloridotetraaquachromium (III) nitrate
    (b) tetraaquadichloridochromium (III) nitrate
    (c) tetraaquadichloridochromium (IV) nitrito
    (d) dichloridotetraaquachromium (IV) nitrito.

45. Which of the following will undergo Cannizzaro reaction?
    (a) Formaldehyde
    (b) Benzaldehyde
    (c) Furfural
    (d) All of these.

46. If one strand of a DNA has the sequence TAGCAACT, the sequence in the complementary strand would be
    (a) ATCGTTGA
    (b) GCTAATCA
    (c) ATGCTTCA
    (d) CGATTAGT

47. The limiting line in Balmer series will have a frequency of
    (a) $6.22 \times 10^{15} s^{-1}$
    (b) $7.22 \times 10^{14} s^{-1}$
    (c) $8.22 \times 10^{14} s^{-1}$
    (d) $9.22 \times 10^{14} s^{-1}$

48. Which one of the following gives a red precipitate with ammoniacal solution of cuprous chloride?
    (a) $CH_3C \equiv CCH_3$
    (b) $H_2C = CH_2$
    (c) $CH_3 — CH_3$
    (d) $HC \equiv CH$

49. van't Hoff factor, i for glucose is
    (a) 0
    (b) 1
    (c) 6
    (d) 2.5

50. In a face-centred cubic arrangement of A and B atoms, A atoms are at the corner of the unit cell and B atoms at the face centres. One of the A atom is missing from one corner in unit cell. The simplest formula of compound is
    (a) A_7B_3
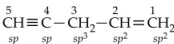   (b) AB_3
    (c) A_7B_{24}
    (d) $A_{7/8}B_6$

1. **(c)**: SI unit of viscosity coefficient is N s m^{-2} or Pa s or decapoise.

   1 poise = 1 g cm^{-1} s^{-1} = 10^{-1} kg m^{-1} s^{-1}

   1 kg m^{-1} s^{-1} = 10 poise = decapoise

2. **(a)**: Triclinic unit cell, $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$.

3. **(d)**: When both double and triple bonds are present at equivalent positions, double bond is always given preference over triple bond while numbering the carbon chain.

$$\overset{5}{CH} \equiv \overset{4}{C} - \overset{3}{CH_2} - \overset{2}{CH_2} = \overset{1}{CH_2}$$
$$\quad sp \quad sp \quad sp^3 \quad sp^2 \quad sp^2$$

   C_2—C_3 bond is formed by overlapping of sp^2 – sp^3 hybrid orbitals.

4. **(c)**: $[Fe(C_2O_4)_3]^{3-}$ is the most stable complex due to chelate formation as $C_2O_4^{2-}$ is a bidentate chelating ligand.

5. **(a)**: Mass of solution = Volume × Density
   $$= 1.5 \text{ mL} \times 3.12 \text{ g mL}^{-1}$$
   $$= 4.68 \text{ g} = 4.7 \text{ g}$$
   (in correct significant figures)

6. **(d)**: The basicity of *o*-, *m*- and *p*-toluidine relative to aniline follows the order:

   p-Toluidine *m*-Toluidine Aniline *o*-Toluidine
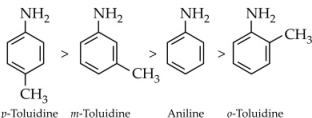
   o-Toluidine is the weakest base due to *ortho*-effect. Due to electron donating effect of CH$_3$— group (+I effect and hyperconjugation effect), both *p*-and *m*-toluidine are stronger bases than aniline. *m*-Toluidine is a weaker base than *p*-toluidine because CH$_3$— group cannot exert hyper-conjugation effect from *m*-position.

7. **(a)**: CrO_2 : $x - 4 = -1 \Rightarrow x = +3$

   ClO_3^- : $x - 6 = -1 \Rightarrow x = +5$

   CrO_4^{2-} : $x - 8 = -2 \Rightarrow x = +6$

   MnO_4^- : $x - 8 = -1 \Rightarrow x = +7$

8. **(b)**: $\Lambda^\circ_{Ba(OH)_2} = \Lambda^\circ_{Ba^{2+}} + 2\Lambda^\circ_{OH^-}$
   $$= 523.28 \text{ S cm}^2 \text{ mol}^{-1} \qquad \ldots(i)$$
   $\Lambda^\circ_{BaCl_2} = \Lambda^\circ_{Ba^{2+}} + 2\Lambda^\circ_{Cl^-} = 280.0 \text{ S cm}^2 \text{ mol}^{-1} \quad \ldots(ii)$
   $\Lambda^\circ_{NH_4Cl} = \Lambda^\circ_{NH_4^+} + \Lambda^\circ_{Cl^-} = 129.8 \text{ S cm}^2 \text{ mol}^{-1} \quad \ldots(iii)$

Now, by (iii) $-\dfrac{1}{2}$ (ii) $+\dfrac{1}{2}$ (i), we get

$$\Lambda^\circ_{NH_4^+} + \Lambda^\circ_{Cl^-} - \frac{1}{2}\Lambda^\circ_{Ba^{2+}} - \Lambda^\circ_{Cl^-} + \frac{1}{2}\Lambda^\circ_{Ba^{2+}} + \Lambda^\circ_{OH^-}$$
$$= \Lambda^\circ_{NH_4OH}$$

$$\Lambda^\circ_{NH_4OH} = \Lambda^\circ_{NH_4Cl} - \frac{\Lambda^\circ_{BaCl_2}}{2} + \frac{\Lambda^\circ_{Ba(OH)_2}}{2}$$

$$= 129.8 - \frac{280.0}{2} + \frac{523.28}{2}$$

$$= 129.8 - 140.0 + 261.64$$

$$= 251.44 \text{ S cm}^2 \text{ mol}^{-1}$$

9. **(d)**:
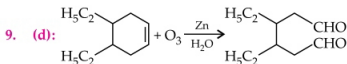
10. **(b)**: Molality = $\dfrac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$

11. **(a)**: Higher the value of $(n + l)$, higher is the energy. When $(n + l)$ value is the same, higher the value of n, higher is the energy.

   $(n + l):$ (4 + 1) (4 + 0) (3 + 2) (3 + 1)

   $\qquad\qquad$ (i) $\qquad$ (ii) $\qquad$ (iii) $\qquad$ (iv)

   $\therefore$ (iv) < (ii) < (iii) < (i)
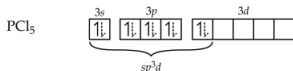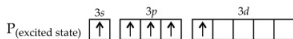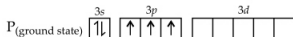
12. **(b)**:

   Trigonal bipyramidal
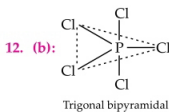
   $_{15}$P = 2, 8, 5
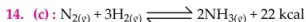
   $$X = \frac{1}{2}[VE + MA - c + a]$$

   $$= \frac{1}{2}[5 + 5 - 0 + 0] = 5 = 5 \text{ hybrid orbitals} = sp^3d$$

   Alternatively on the basis of valence bond approach:

13. **(d)**

14. (c) : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 22$ kcal
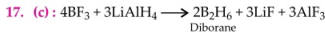
As the forward reaction is exothermic and leads to lowering in pressure thus, according to Le Chatelier's principle, low temperature and high pressure will produce $NH_{3(g)}$ in good yield.

15. (a)

16. (a) : Aldehydes and ketones having at least one α-hydrogen atom undergo aldol condensation.

17. (c) : $4BF_3 + 3LiAlH_4 \longrightarrow \underset{\text{Diborane}}{2B_2H_6} + 3LiF + 3AlF_3$

18. (c) : Barbituric acid and its derivatives are tranquilizers and precisely to say hypnotic tranquilizers.

19. (c) : Sodium hexametaphosphate, $Na_2[Na_4(PO_3)_6]$ or $Na_6P_6O_{18}$, commercially called 'calgon' is used to remove permanent hardness of water.

20. (c) : Peroxyacetyl nitrate (PAN) formed from the primary pollutants NO_2, O_3 and hydrocarbons, is the secondary pollutant.

21. (d) : Tenth element is neon which is a member of noble gases (group 18 or zero). The atomic numbers of other elements of this group are 2 (He), 18 (Ar), 36 (Kr), 54 (Xe) and 86 (Rn).

22. (a) : Buna-S is an addition copolymer of 1,3-butadiene and styrene. Nylon-2,6 is a condensation copolymer of glycine and aminocaproic acid. Alkyd resin is a condensation copolymer of ethylene glycol and terephthalic acid. PTFE (Polytetrafluoroethylene) or Teflon is an addition homopolymer of tetrafluoroethylene.

23. (c) : Same bonds are formed in reactions (i) and (ii) but no bonds are broken in reaction (i) whereas bonds in the reactant molecules are broken in reaction (ii). As some energy is absorbed or used up to break the bonds in reaction (ii), energy of reaction (i) is greater than that of reaction (ii), *i.e.*, $x > y$.

24. (a) :

$$\overset{7}{CH_3} - \overset{6}{CH} - \overset{5}{CH_2} - \overset{4}{CH} - \overset{3}{CH_2} - \overset{2}{CH} - \overset{1}{CH_2} - OH$$

with Br, CH_2CH_3, Br substituents

2, 6-Dibromo-4-ethylheptan-1-ol

25. (b):

Linear   Linear
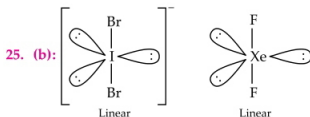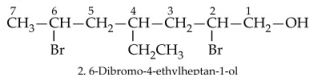
26. (a) : Due to small size, high electronegativity and high ionization enthalpy of Be, $BeCl_2$ is covalent and hence soluble in organic solvents such as ethanol.

27. (b)

28. (c) : Physisorption is reversible in nature.

29. (b): Ti^{3+} and Cu^{2+} are coloured while Sc^{3+} is colourless due to empty d-orbitals.
Ag^+ and Cd^{2+} are colourless due to completely filled d-orbitals.

30. (d): Al is obtained by electrolytic reduction process.

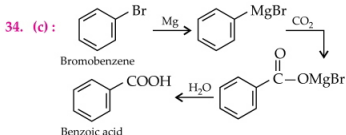**31. (d):** Stability of the molecule is directly proportional to the number of bonding electrons.

32. (c) : Hydrolysis of optically active 2-bromobutane follows S_N1 mechanism, which proceeds with racemisation.
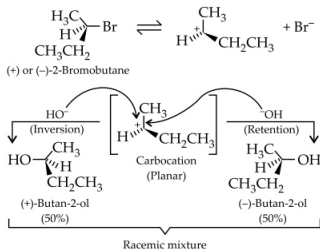
33. (d): It is an example of basic buffer for that

$$pH = pK_a + \log \frac{[\text{Base}]}{[\text{Salt}]}$$

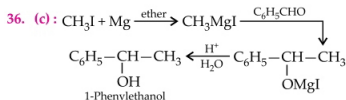$$= 9.26 + \log \frac{0.02}{2 \times 0.01} = 9.26 + \log 1$$

34. (c) :
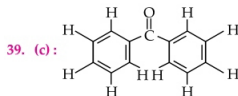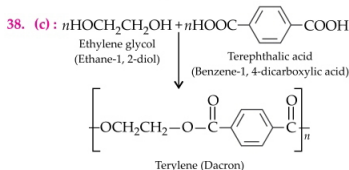

35. (c) : For n^{th} order reaction; $r = k[A]^n$

$$\therefore \quad k = \frac{r}{[A]^n} = \frac{\text{mol } L^{-1} s^{-1}}{(\text{mol } L^{-1})^n}$$

$$= \text{mol}^{1-n} L^{n-1} s^{-1}$$

36. (c) : $CH_3I + Mg \xrightarrow{ether} CH_3MgI \xrightarrow{C_6H_5CHO}$

$$C_6H_5-CH-CH_3 \xleftarrow[H_2O]{H^+} C_6H_5-CH-CH_3$$
$$\underset{\underset{\text{1-Phenylethanol}}{OH}}{|} \qquad\qquad \underset{OMgI}{|}$$

37. (d) : In acidic medium,

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

The reaction shows gain of $5e^-$ *i.e.* reduction.

38. (c) : $nHOCH_2CH_2OH + nHOOC-\!\!\!\!\bigcirc\!\!\!\!-COOH$

Ethylene glycol
(Ethane-1, 2-diol)

Terephthalic acid
(Benzene-1, 4-dicarboxylic acid)

$$\left[-OCH_2CH_2-O-\overset{O}{\overset{||}{C}}-\!\!\!\!\bigcirc\!\!\!\!-\overset{O}{\overset{||}{C}} \right]_n$$

Terylene (Dacron)

39. (c) :

40. (d) : Only 1° amides undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amide, therefore, it does not undergo Hofmann bromamide reaction.

41. (d)

42. (b) :

sp^3 orbital with lone pair of electrons

sp^2-hybridised
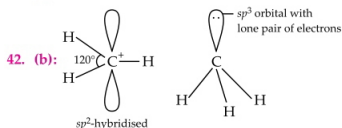
43. (b)   44. (b)

45. (d) : Carbonyl compounds which do not contain α-hydrogen atom when treated with strong alkali undergo self oxidation-reduction or disproportionation reaction.

46. (a) : Two strands of DNA are antiparallel and complementary to each other.

If one strand has the sequence TAGCAACT then the sequence in the complementary strand would be ATCGTTGA.

47. (c) : The limiting line of Balmer series refers to the transition of electron from ∞ to 2nd orbit.

$$\upsilon = c.\bar{\upsilon}$$

$$= 3\times10^{10}\,cm\,s^{-1}\times109677\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)cm^{-1}$$

$$= 3.29\times10^{15}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)sec^{-1}\;(\because\;n_1=2, n_2=\infty)$$

$$= 8.22\times10^{14}\,s^{-1}$$

48. (d) : The H-atom of acetylene and terminal alkynes are weakly acidic. Due to acidic nature of the H-atoms attached to a triple bond, acetylenes and terminal alkynes form red ppt. of copper acetylides with ammoniacal cuprous chloride.

$$CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow CuC \equiv CCu$$
$$\underset{\text{Red ppt.}}{}$$
$$+ 2NH_4Cl + 2H_2O$$
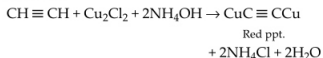
49. (b) : van't Hoff factor, i for non electrolyte solution is one.

50. (c) : No. of atoms of A at the corners = 7

($\because$ one A atom is missing.)

$\therefore$ Contribution by atoms of A towards unit cell

$$= 7\times\frac{1}{8} = \frac{7}{8}$$

No. of atoms of B at face-centres = 6

$\therefore$ Contribution by atoms of B towards unit cell

$$= 6\times\frac{1}{2} = 3$$

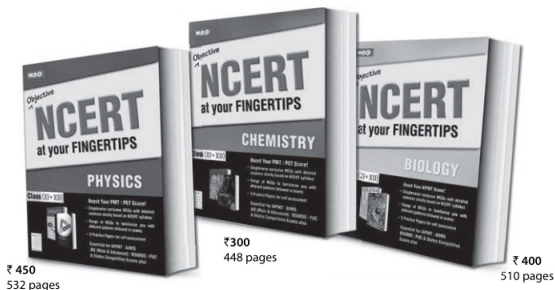Thus, $A : B = 7/8 : 3$ or $7 : 24$

Thus, formula is A_7B_{24}.

AIPMT Special

1. The type of crystal defect indicated by the given diagram and its effect on the density is

(a) Frenkel defect, Density will decrease
(b) Schottky defect, Density does not change
(c) Frenkel defect, Density does not change
(d) Metal excess defect, Density will increase.

2. The reaction $R \longrightarrow P$ whose Q_c and K_c are related as shown in the figure will proceed in

(a) reverse direction
(b) forward direction
(c) no reaction occurs
(d) can't be predicted.

3. Which of the following is correct for cyclopenta-diene?
(a) Aromatic, $n = 2$
(b) Non-aromatic, $n = 2$
(c) Aromatic, $n = 0.5$
(d) Non-aromatic, $n = 0.5$

4. Acetaldehyde on treatment with few drops of concentrated sulphuric acid gives
(a) ethene
(b) ethyne
(c) acetophenone
(d) paraldehyde.

5. Thomas slag is prepared by reaction between
(a) MnO and SiO_2
(b) CaO and SiO_2
(c) CaO and P_4O_{10}
(d) FeO and SiO_2

6. Which of the following compounds on reaction with CH_3MgBr will give a tertiary alcohol?

(a) C_6H_5CHO
(b) $C_2H_5CO_2CH_3$
(c) C_2H_5COOH
(d) $CH_3CH{\longrightarrow}CHCH_3$
$\underset{O}{\diagdown}$

7. Which of the following is a coloured ion?
(a) $[Cr(H_2O)_6]^{3+}$
(b) $[Cu(CN)_4]^{3-}$
(c) $[Ti(H_2O)_6]^{4+}$
(d) $[Sc(H_2O)_6]^{3+}$

8. Identify the amino acid having basic side chain.
(a) Lysine
(b) Alanine
(c) Proline
(d) Leucine

9. A bulb emits light of wavelength 4500 Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?
(a) 1.432×10^{18}
(b) 3.658×10^{20}
(c) 5.487×10^{17}
(d) 2.727×10^{19}

10. Out of the following, which one is matched incorrectly?
(a) $1\,N = 1\,kg\,m\,s^{-2}$
(b) $1\,V = kg\,m^2\,s^{-2}\,A^{-1}$
(c) $1\,J = 1\,kg\,m^2\,s^{-2}$
(d) $1\,Pa = 1\,kg\,m^{-1}\,s^{-2}$

11. Perlon is a polymer of
(a) phenol
(b) ethylene dichloride
(c) caprolactam
(d) none of these.

12. Carbon tetrachloride when treated with phenol in the presence of aqueous sodium hydroxide at 340 K followed by hydrolysis gives
(a) salicylaldehyde
(b) salicylic acid
(c) both of these
(d) none of these.

13. Aniline on heating with acidified potassium dichromate solution gives a yellow coloured compound. The compound is
(a) nitrobenzene
(b) nitrosobenzene
(c) p-benzoquinone
(d) p-aminophenol.

14. Pick up the incorrect statement.
(a) Asbestos and willemite are silicate minerals.
(b) Anglesite and barytes are sulphate minerals.
(c) Sylvine and fluorspar are halide minerals.
(d) Calamine and sphalerite are the minerals of calcium.

15. Tautomerism is not exhibited by

(a) [structure: benzene ring]—CH=CH—OH

(b) [structure: cyclohexadiene dione with two O]

(c) [structure: cyclohexanone type with O at bottom and O]   (d) [structure: cyclohexanone with =O]
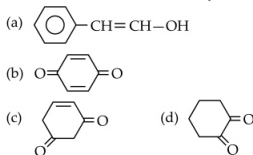
16. For the following reaction occurring in an automobile $2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$; the sign of ΔH, ΔS and ΔG would be
(a) −, +, +   (b) +, +, −
(c) +, −, +   (d) −, +, −

17. Among LiCl, BeCl$_2$, BCl$_3$ and CCl$_4$, the covalent bond character follows the order
(a) LiCl < BeCl$_2$ < BCl$_3$ > CCl$_4$
(b) LiCl > BeCl$_2$ < BCl$_3$ < CCl$_4$
(c) LiCl < BeCl$_2$ < BCl$_3$ < CCl$_4$
(d) LiCl > BeCl$_2$ > BCl$_3$ > CCl$_4$

18. Which of the following is an amine hormone?
(a) Insulin   (b) Progesterone
(c) Thyroxine   (d) Oxytocin

19. The data for the reaction $A + B \rightarrow C$, is

Exp.	$[A]_0$	$[B]_0$	Initial rate
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

The rate law corresponds to the above data is
(a) Rate = $k[A][B]^3$ (b) Rate = $k[A]^2[B]^2$
(c) Rate = $k[B]^3$ (d) Rate = $k[B]^4$

20. Which law is indicated by given graph?

[graph: Partial pressure of a gas in vapour phase (y-axis) vs Mole fraction of the gas in solution (x-axis), showing a straight line]
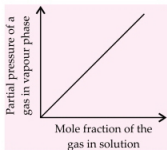
(a) Avogadro's law   (b) Boyle's law
(c) Charles' law   (d) Henry's law

21. On addition of 1 mL of 10% NaCl solution to 10 mL gold sol in the presence of 0.25 g of starch, the coagulation is just prevented. Starch has the gold number

(a) 0.025   (b) 0.25
(c) 2.5   (d) 250

22. Which of the following statements is not correct?
(a) Bond energy of F$_2$ > Cl$_2$
(b) Electronegativity of F > Cl
(c) F is more oxidising than Cl
(d) Electron affinity of Cl > F

23. Two electrochemical cells, Zn | Zn^{2+} || Cu^{2+} | Cu and Fe | Fe^{2+} || Cu^{2+} | Cu are connected in series. What will be the net e.m.f. of the cell at 25°C? Given : $E°$ of Zn^{2+} | Zn = −0.76 V, Cu^{2+} | Cu = +0.34 V, Fe^{2+} | Fe = −0.41 V
(a) +1.85 V   (b) −1.85 V
(c) +0.83 V   (d) −0.83 V

24. The compound formed when malonic acid is heated with urea is
(a) cinnamic acid   (b) butyric acid
(c) barbituric acid   (d) crotonic acid.

25. $CH_3CCH_2CH_2COCH_2CH_3 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr \text{ (one mol)}} 'A'$,
[two C=O groups shown above]
'A' formed in this reaction is

(a) $CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2CH_2-\overset{O}{C}-OCH_2CH_3$

(b) $CH_3-\overset{O}{C}-CH_2CH_2-\overset{O}{C}-CH_3$

(c) [lactone structure with H$_3$C, H$_3$C groups and =O]

(d) $CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$
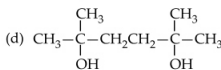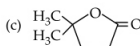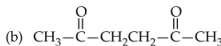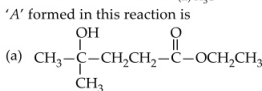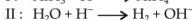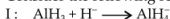
26. Consider the following reactions:
I : $AlH_3 + H^- \longrightarrow AlH_4^-$
II : $H_2O + H^- \longrightarrow H_2 + OH^-$
Select the correct statement from the following:
(a) H$^-$ is a Lewis acid in I and Lewis base in II
(b) H$^-$ is a Lewis base in I and Bronsted base in II.
(c) H$^-$ is a Lewis acid in I and Bronsted base in II
(d) H$^-$ is a Lewis base in I and II.

27. When CuSO$_4$ is electrolysed using platinum electrodes,
(a) copper is liberated at cathode, sulphur at anode
(b) copper is liberated at cathode, oxygen at anode

(c) sulphur is liberated at cathode, oxygen at anode

(d) oxygen is liberated at cathode, copper at anode.

28. $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2, hv} A + B$

    (Monochlorination products)

    The approximate ratio of percentage yields of A and B formed in the above reaction is
    (a) 50 : 50   (b) 28 : 72
    (c) 45 : 55   (d) 60 : 40

29. In the given reaction,
    $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$,
    X is
    (a) a white gelatinous precipitate
    (b) insoluble in excess of NH_4OH
    (c) insoluble in excess of $NaOH$
    (d) acidic in nature.

30. The oxide which cannot act as reducing agent is
    (a) SO_2 (b) NO_2
    (c) CO_2 (d) ClO_2

31. The root mean square velocity at STP for the gases H_2, N_2, O_2 and HBr are in the order
    (a) $H_2 < N_2 < O_2 < HBr$ (b) $HBr < O_2 < N_2 < H_2$
    (c) $H_2 < N_2 = O_2 < HBr$ (d) $HBr < O_2 < H_2 < N_2$

32. If the van der Waals' parameters of two gases are given as

	a/dm^6 bar mol^{-2}	b/dm^3 mol^{-1}
Gas A	6.5	0.056
Gas B	18.0	0.011

    then consider the following statements.
    1. Critical volume of A > Critical volume of B
    2. Critical pressure of A > Critical pressure of B
    3. Critical temperature of A > Critical temperature of B
    Which of the above statement(s) is/are correct?
    (a) 1 alone   (b) 1 and 2
    (c) 1, 2 and 3   (d) 2 and 3
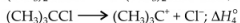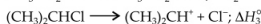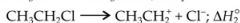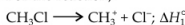
33. For the reaction,
    $CH_3Cl \longrightarrow CH_3^+ + Cl^-; \Delta H_1^\circ$
    $CH_3CH_2Cl \longrightarrow CH_3CH_2^+ + Cl^-; \Delta H_2^\circ$
    $(CH_3)_2CHCl \longrightarrow (CH_3)_2CH^+ + Cl^-; \Delta H_3^\circ$
    $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-; \Delta H_4^\circ$
    The correct order of enthalpies of ionization is
    (a) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ > \Delta H_4^\circ$
    (b) $\Delta H_1^\circ < \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$
    (c) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ < \Delta H_4^\circ$
    (d) $\Delta H_1^\circ > \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$

34. $PhCH_2MgBr + CH_3CH{=}O \longrightarrow$

    $PhCH_2-\overset{\overset{OH}{|}}{CH}-CH_3 + 'P'$
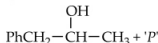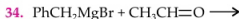
    'P' is the isomer of other given product. The by-product 'P', is

    (a) $CH_2CH_2CH_2OH$

    (b) $\overset{\overset{OH}{|}}{CH}-CH_2CH_3$

    (c) with CH_3 and $\overset{\overset{}{}}{CH}-CH_3$ with OH

    (d) $CH_2OCH_2CH_3$
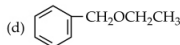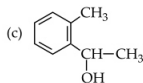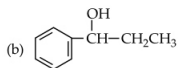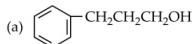
35. The correct order of acidity of the following compounds is
    $\underset{I}{C_6H_5COOH} \quad \underset{II}{CH_3CH_2OH} \quad \underset{III}{C_6H_5OH} \quad \underset{IV}{CH_3COOH}$
    (a) III < II < I < IV   (b) IV < I < III < II
    (c) II < III < I < IV   (d) I < II < III < IV
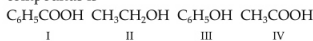
36. Four diatomic species are listed below in different sequences. Which of these represents the correct order of their increasing bond order?
    (a) $C_2^{2-} < He_2^+ < NO < O_2^-$
    (b) $He_2^+ < O_2^- < NO < C_2^{2-}$
    (c) $O_2^- < NO < C_2^{2-} < He_2^+$
    (d) $NO < C_2^{2-} < O_2^- < He_2^+$

37. Which complex is likely to show optical activity?
    (a) $trans$-$[Co(NH_3)_4Cl_2]^+$
    (b) $[Cr(H_2O)_6]^{3+}$
    (c) cis-$[Co(NH_3)_2(en)_2]^{3+}$
    (d) $trans$-$[Co(NH_3)_2(en)_2]^{3+}$

38. Which of the following ions is paramagnetic?
    (a) $[Ni(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{4-}$
    (c) $[Ni(CO)_4]$ (d) $[Ni(CN)_4]^{2-}$

39. The van der Waals' constants for four gases P, Q, R and S are 4.17, 3.59, 6.71 and 3.8 atm L^2 mol^{-2}. Therefore, the ascending order of their liquefaction is
    (a) $R < P < S < Q$ (b) $Q < S < R < P$
    (c) $Q < S < P < R$ (d) $R < P < Q < S$

40. A metal oxide has the formula Z_2O_3. It can be reduced by hydrogen to give free metal and water. 0.1596 g of the metal oxide requires 6 mg of hydrogen for complete reduction. The atomic weight of the metal is
   (a) 27.9   (b) 159.6
   (c) 79.8   (d) 55.8

41. In the cyanide process for extraction of gold and silver from ores, the cyanide solution acts as a
   (a) reducing agent to reduce the gold and silver compounds present in the ores into the metallic states
   (b) leaching agent to bring the gold and silver into solution as cyanide complexes and thus separate these metals from the ores
   (c) leaching agent to dissolve all the other constituents of the ores leaving the gold and silver as metals
   (d) leaching agent to bring the ores into solution.

42. Which of the following statements is false?
   (a) Strontium decomposes water readily than beryllium.
   (b) Barium carbonate melts at a higher temperature than calcium carbonate.
   (c) Barium hydroxide is more soluble in water than magnesium hydroxide.
   (d) Beryllium hydroxide is more basic than barium hydroxide.

43. Which of the following statements about H_3BO_3 is not correct?
   (a) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds.
   (b) It does not act as proton donor but acts as a Lewis acid by accepting hydroxyl ion.
   (c) It is a strong tribasic acid.
   (d) It is prepared by acidifying an aqueous solution of borax.

44. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their main ionic radii.
   (a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
   (b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
   (c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
   (d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

45. The methods chiefly used for the extraction of lead and tin from their main ores are respectively
   (a) self reduction and carbon reduction
   (b) carbon reduction and self reduction
   (c) cyanide process and carbon reduction
   (d) none of these.

SOLUTIONS

1. **(c)** : Defect shown in the diagram is Frenkel defect in which smaller ion (usually cation) is dislocated from its normal site to a interstitial site. It does not change the density of the solid.

2. **(a)** : In the given case, $Q_c > K_c$, the reaction $R \rightarrow P$ will proceed in the direction of reactants *i.e.*, in reverse direction ($k_f < k_b$).

3. **(d)** :

   Cyclopentadiene consists of two double bonds *i.e.*, 4π electrons and is non planar. According to Huckel's rule, molecule should contain $(4n + 2)\pi$ electrons
   $\Rightarrow 4n + 2 = 4 \Rightarrow n = 0.5$
   This value is not an integer hence, it is non-aromatic.

4. **(d)** : $3CH_3CHO \xrightarrow[\text{dil. } H_2SO_4]{\text{conc. } H_2SO_4} (CH_3CHO)_3$
   $\underset{\text{Acetaldehyde}}{} \qquad \underset{\text{Paraldehyde}}{}$

   It is a cyclic trimer represented as
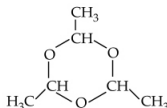
5. **(c)** : $6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$
   $\underset{\text{Thomas slag}}{}$

6. **(b)** : Ester reacts with Grignard's reagent to form a ketone which at once reacts with more of Grignard's reagent to give 3° alcohol.

7. **(a)** : $Cr^{3+} \rightarrow 3d^3$, can undergo *d-d* transition.
   In $Cu^+ \rightarrow 3d^{10}$; Ti^{4+}, $Sc^{3+} \rightarrow 3d^0$, *d-d* transitions are not possible.

8. **(a)** : $H_2N-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle NH_2}{|}}{CH}-COOH$
   $\underset{\text{Lysine}}{}$

9. **(d)** : Power = Energy per second
   150 watt = 150 J per second
   $\therefore \quad E = 150$ J

   Energy emitted as light = $\dfrac{150 \times 8}{100} = 12$ J

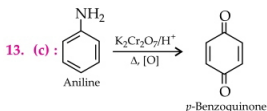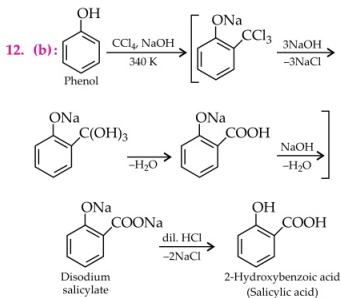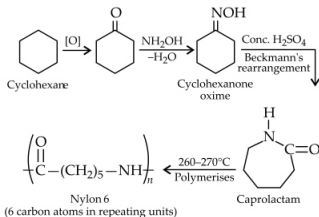   Radiant energy = $\dfrac{nhc}{\lambda}$

$$n = \frac{\text{Radiant energy} \times \lambda}{hc}$$

$$n = \frac{12 \times 4500 \times 10^{-10}}{6.6 \times 10^{-34} \times 3 \times 10^8} = 2.727 \times 10^{19} \text{ photons}$$

**10. (b) :** Potential difference $= \dfrac{\text{Energy}}{\text{Charge}}$

$$1 \text{ V} = \frac{1 \text{ J}}{1 \text{ C}} = \frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ A s}} = 1 \text{ kg m}^2 \text{ s}^{-3} \text{A}^{-1}$$

11. (c) : Perlon is the another name of nylon 6 which is a polymer of caprolactam.

Cyclohexane   Cyclohexanone oxime

Nylon 6
(6 carbon atoms in repeating units)   Caprolactam

12. (b) :

Phenol

Disodium
salicylate   2-Hydroxybenzoic acid
(Salicylic acid)

13. (c) :

Aniline   p-Benzoquinone

14. (d) : Calamine is $ZnCO_3$ and sphalerite or zinc blende is ZnS. Both are minerals of zinc.

15. (b) : (a) shows tautomerism since aldehydes are more stable than vinyl alcohols.

$$C_6H_5-CH=CH-OH \rightleftharpoons C_6H_5CH_2CHO$$
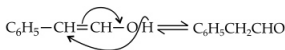
(c) shows tautomerism because enolic form is stabilized by aromatic character.

Resorcinol
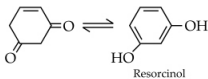
(d) shows tautomerism as enolic form is stabilized by H-bonding.
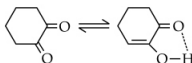
(b) does not show tautomerism because it does not have α-hydrogen atoms at the saturated carbon atom.

16. (d) : (i) The given reaction is a combustion reaction, always exothermic. Hence, ΔH is negative.
(ii) Since there is a increase in the number of gaseous moles, therefore ΔS is positive.
(iii) $\Delta G = \Delta H - T\Delta S$; ΔG is negative.

17. (c) : Along the period, electronegativity increases as we move from, Li $\to$ Be $\to$ B $\to$ C, hence electronegativity difference between the element and Cl decreases and accordingly, the covalent character increases. Thus, $LiCl < BeCl_2 < BCl_3 < CCl_4$ is the correct order of covalent bond character.

18. (c) : Thyroxine and adrenaline are amine hormones. Thyroxine produced in the thyroid gland is an iodinated derivative of amino acid tyrosine.

19. (c) : $A + B \to C$
Let rate $= k[A]^x [B]^y$
where order of reaction is $(x + y)$
Putting the values of exp. 1, 2, and 3, we get following equations.

$$0.10 = k [0.012]^x [0.035]^y \qquad ...(i)$$
$$0.80 = k [0.024]^x [0.070]^y \qquad ...(ii)$$
$$0.10 = k [0.024]^x [0.035]^y \qquad ...(iii)$$

Dividing eq. (ii) by eq. (iii), we get

$$\frac{0.80}{0.10} = \left(\frac{0.070}{0.035}\right)^y \Rightarrow 2^y = 8 \Rightarrow y = 3$$

Keeping $[A]$ constant, $[B]$ is doubled, rate becomes 8 times.

Dividing eq. (iii) by eq. (i), we get

$$\frac{0.10}{0.10} = \left(\frac{0.024}{0.012}\right)^x \Rightarrow 2^x = 1 \Rightarrow x = 0$$

Keeping $[B]$ constant, $[A]$ is doubled, rate remains unaffected. Hence rate is independent of $[A]$.
Rate $\propto [B]^3$

20. **(d)**: Henry's law states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" and is expressed as

$$p = K_H x$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, a straight line plot passing through the origin is obtained with slope = K_H (in atm or bar).

21. **(d)**: By definition, gold number of starch is the amount of starch in milligrams added to 10 mL of standard gold sol which prevents the coagulation of gold on adding 1 mL of 10% NaCl solution. So, the amount of starch is 0.25 g = 250 mg. Hence gold number is 250.

22. **(a)**: Due to more repulsion between the non-bonding electron pairs ($2p$) of two fluorine atoms (due to small size of F-atom) in comparison to non-bonding electron pairs ($3p$) in chlorine, the bond energy of F_2 is less than Cl_2.
B.E. (F_2) = 158.8 kJ/mol and
B.E. (Cl_2) = 242.6 kJ/mol.

23. **(a)**: EMF for the cell, Zn | Zn^{2+} || Cu^{2+} | Cu
$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} = +0.34 - (-0.76) = 1.10$ V
EMF for the cell, Fe | Fe^{2+} || Cu^{2+} | Cu
$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Fe^{2+}/Fe} = +0.34 - (-0.41$ V) = 0.75 V
Since the two cells are connected in series, therefore, the net EMF of the two cells
= 1.10 + 0.75 = +1.85 V

24. **(c)**:
Malonic acid

Barbituric acid
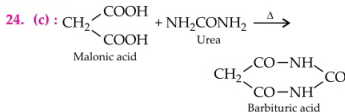
25. **(c)**: Of the two carbonyl groups in the starting material, the ketone carbonyl is more reactive than the ester (the ester carbonyl is stabilized by electron release from oxygen).
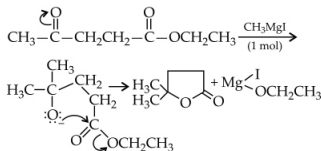
26. **(b)**: H^- ion is a Lewis base in I and Bronsted base in II as Lewis base is electron pair donor. Bronsted base is proton acceptor.
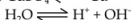
27. **(b)**: $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$
$H_2O \rightleftharpoons H^+ + OH^-$
At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

28. **(b)**: The relative ratio of these two isomeric chlorobutanes can be easily calculated by knowing the number and type of hydrogens (1°, 2° or 3°) to be substituted and their relative reactivity which is in the order 1 : 3·8 : 5 for chlorination at 298 K.
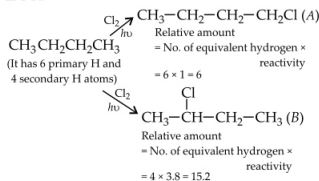
Total amount = 6 + 15.2 = 21.2

$$\% \text{ of } A = \frac{6}{21.2} \times 100 = 28.3$$

$$\% \text{ of } B = \frac{15.2}{21.2} \times 100 = 71.7$$

29. **(a)**: $Al_2(SO_4)_3$ reacts with NH_4OH to form a white gelatinous precipitate of $Al(OH)_3$ (X) which is soluble in excess of NH_4OH or NaOH.
$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$
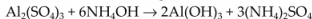
30. **(c)**: CO_2 cannot act as reducing agent since it cannot accomodate an oxidation state of more than +4.

31. **(b)**: We know, $PV = \dfrac{1}{3}mnu^2 = \dfrac{1}{3}Mu^2$

or $u = \sqrt{3PV/M}$

At STP, $u \propto \sqrt{\dfrac{1}{M}}$

and molecular masses of H_2, N_2, O_2 and HBr are 2, 28, 32 and 81.

Thus, the correct order of root mean square velocity is $HBr < O_2 < N_2 < H_2$.

32. (a) : For Gas A,

$V_c = 3b = 3 \times 0.056 = 0.168$ dm^3 mol^{-1}

$$P_c = \frac{a}{27b^2} = \frac{6 \cdot 5}{27 \times (0 \cdot 056)^2} = 76 \cdot 8 \text{ atm}$$

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 6 \cdot 5}{27 \times 0 \cdot 0821 \times 0 \cdot 056} = 418.9 \text{ K}$$

For Gas B,

$V_c = 3 \times 0.011 = 0.033$ dm^3 mol^{-1}

$$P_c = \frac{18.0}{27 \times (0.011)^2} = 5509.6 \text{ atm}$$

$$T_c = \frac{8 \times 18}{27 \times 0.0821 \times 0.011} = 5905.6 \text{ K}$$

33. (a) : The stability of carbonium ions has the following order

$$\overset{+}{C}H_3 < CH_3 - \overset{+}{C}H_2 < CH_3 - \overset{+}{C}H < CH_3 - \overset{+}{C} +$$

with CH_3 and CH_3 groups
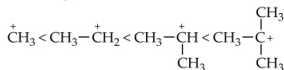
therefore, the formation of $\overset{+}{C}H_3$ requires more heat and ΔH_1° (the enthalpy of ionization of CH_3Cl) will be maximum and ΔH_4° is minimum.

34. (c) :
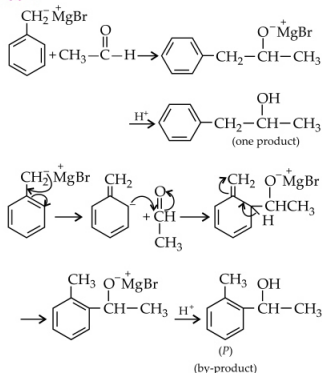
35. (c) : Carboxylic acids are stronger acids than alcohols and phenols.

Among carboxylic acids, aliphatic acids are stronger acids than aromatic acids.

Phenols are stronger acids than alcohols.

36. (b) : According to molecular orbital theory, the energy level of the given molecules are

$C_2^{2-} \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$

B.O. = 1/2[10 − 4] = 3

$He_2^+ \rightarrow \sigma 1s^2\ \sigma^* 1s^1$

B.O. = 1/2[2 − 1] = 1/2 = 0.5

$NO \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1$

B.O. = 1/2[10 − 5] = 2.5

$O_2 \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$
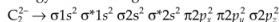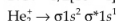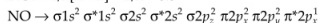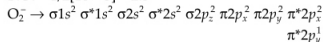
B.O. = 1/2[10 − 7] = 1.5

So, the correct order of their increasing bond order is $He_2^+ < O_2 < NO < C_2^{2-}$

37. (c) : Octahedral complexes of the type Ma_6 does not show geometrical and optical isomerism.
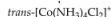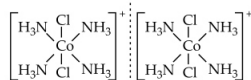
trans-[Co(NH$_3$)$_4$Cl$_2$]$^+$
Superimposable mirror images
(Optically inactive)
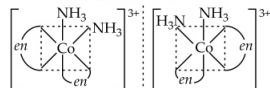
cis-[Co(NH$_3$)$_2$(en)$_2$]$^{3+}$
Non-superimposable mirror images
(Optically active)
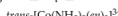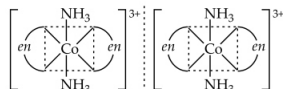
trans-[Co(NH$_3$)$_2$(en)$_2$]$^{3+}$
Superimposable mirror images
(Optically inactive)

38. (a) : In [Ni(CO)$_4$],
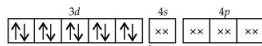
sp^3 (four pairs from four CO ligands)

In $[Ni(CN)_4]^{2-}$,

dsp^2 (four pairs from
for CN$^-$ ligands)

In $[Fe(CN)_6]^{4-}$,

d^2sp^3 hybridisation
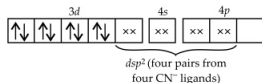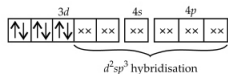
Strong field ligands like CO, CN$^-$ generally result in inner orbital complexes.

In $[Ni(H_2O)_6]^{2+}$, H_2O is a weak field ligand, pairing of electrons will not take place.

Hence $[Ni(H_2O)_6]^{2+}$ is paramagnetic in nature.

39. (c) : Easily liquefiable gases have greater intermolecular forces which is represented by high value of a. The greater the value of a more will be the liquefiability. So, the order is $Q < S < P < R$.

40. (d) : $Z_2O_3 + 3H_2 \rightarrow 2Z + 3H_2O$

Valency of metal in Z_2O_3 = +3

0.1596 g of Z_2O_3 reacts with 6 mg of H_2

$\therefore$ 1 g of H_2 reacts with $\dfrac{0.1596}{0.006}$

$= 26.6$ g of Z_2O_3

$\therefore$ Eq. wt. of Z_2O_3 = 26.6

Now, Eq. wt. of Z + Eq. wt. of O

$=$ Eq. wt. of $Z + 8 = 26.6$

$\Rightarrow$ Eq. wt. of $Z = 26.6 - 8 = 18.6$

$\therefore$ At. wt. of $Z = 18.6 \times 3 = 55.8$

$$\left[\text{Eq. wt.} = \frac{\text{Atomic wt.}}{\text{Valency of metal}} \right]$$

41. (b) : Leaching is used for extracting precious metals like silver and gold by converting these metals or their ores into their soluble cyanide complexes. This method is also called Mac-Arthur Forest cyanide process.

$4M + 8CN^- + 2H_2O + O_2 \rightarrow 4[M(CN)_2]^- + 4OH^-$

(air)   Soluble complex
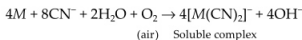
From soluble complex, the metal is obtained by replacement with electropositive metal like zinc.

$2[M(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2M$
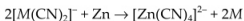
42. (d) : Basic strength of alkaline earth metal hydroxides increases down the group because of increase in ionic size and decrease in ionization enthalpy.

43. (c) : H_3BO_3 is a weak monobasic acid. We know that $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$. Therefore it is a weak monobasic acid.

44. (a) : Ionic radii of lanthanoids decrease across the series due to lanthanoid contraction. Thus, order of ionic radii is

$La^{3+} > Ce^{3+} > Pm^{3+} > Yb^{3+}$

45. (a) : Lead is extracted by self reduction from its most important ore PbS (Galena) in which sulphide ore is changed to oxide or sulphate which then reacts with remaining part to give metal and sulphur dioxide.

Tin is extracted by carbon reduction from its ore SnO_2 (Tinstone) in which carbon combines with oxygen of metal oxide to form CO.
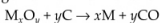
$M_xO_y + yC \rightarrow xM + yCO$
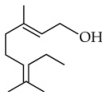
PRACTICE PAPER 2Q14

JEE Advanced

PAPER-I

SECTION-I
#### Only One Option Correct Type

This section contains 10 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. The IUPAC name of the following compound is

   (a) 3-ethyl-2, 6-dimethyloct-2, 6-dien-1-ol
   (b) 6-ethyl-3-methyl-6-propyloct-2-en-1-ol
   (c) 6-ethyl-3, 7-dimethyloct-2, 6-dien-1-ol
   (d) 3-ethyl-5, 8-dimethyloct-3, 7-dien-1-ol.

2. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25°C) and are interconnected through a salt bridge. The emf of the cell is
   (a) 0.21 V   (b) 0.059 V
   (c) 0.018 V   (d) 0.021 V

3. Consider the following complex,
   $$Na[Cr(NH_3)_2(ox)_2]\cdot 3H_2O$$
   The coordination number, oxidation number, number of d-electrons, number of unpaired d-electrons on the metal and magnetic moment (in B.M.) are respectively
   (a) 6, + 2, 4, 0,0   (b) 4, + 3, 3, 3.87
   (c) 6, + 3, 3, 3, 3.87   (d) 4, + 2, 4, 0,0

4. The bond lengths of N_2^+, N_2^{2-}, N_2 and N_2^- species are in the order
   (a) $N_2 > N_2^- = N_2^+ > N_2^{2-}$ (b) $N_2^{2-} > N_2^+ > N_2^- > N_2$
   (c) $N_2^{2-} > N_2^- > N_2 > N_2^+$ (d) $N_2^{2-} > N_2^+ = N_2^- > N_2$

5. X and Y are two elements which form X_2Y_3 and X_3Y_4. If 0.20 mol of X_2Y_3 weighs 32.0 g and 0.4 mol of X_3Y_4 weighs 92.8 g, the atomic weights of X and Y are respectively
   (a) 16.0 and 56.0   (b) 8.0 and 28.0
   (c) 56.0 and 16.0   (d) 28.0 and 8.0

6. $(X) \xrightarrow{\text{dil. NaOH}} (Y) \xrightarrow{\Delta}$

   $\xrightarrow{\text{LiAlH}_4} (Z)$
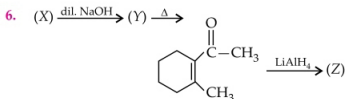
   X, Y and Z in the above reaction are respectively

   (a)

   (b) $CH_3CO(CH_2)_5COCH_3$,

   (c) $CH_3CO(CH_2)_4COCH_3$,

(d)
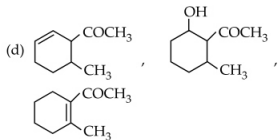
7. The correct order of the increasing s character of the orbital of B which overlaps with the orbital of F to form B − F bond in BF_2^+, BF_3 and BF_4^- is
(a) $BF_2^+ < BF_4^- < BF_3$
(b) $BF_3 < BF_2^+ < BF_4^-$
(c) $BF_2^+ < BF_3 < BF_4^-$
(d) $BF_4^- < BF_3 < BF_2^+$

8. In cyclotrimetaphosphoric acid, number of $P − O − P$ bonds, $P = O$ bonds and $P − OH$ bonds are respectively
(a) 6, 3, 3   (b) 5, 0, 3   (c) 4, 3, 0   (d) 3, 3, 3

9. NH_3 acts as an acid in
(a) $NH_3 + HCl \rightarrow NH_4Cl$
(b) $NH_3 + H^+ \rightarrow NH_4^+$
(c) $NH_3 + Na \rightarrow NaNH_2 + H^+$
(d) NH_3 cannot act as acid.

10. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4

11. Which of the following conditions indicate the spontaneity of a reaction?
(a) ΔH = +ve ΔS = +ve, at low temperature
(b) ΔH = +ve ΔS = +ve, at high temperature
(c) ΔH = −ve ΔS = −ve, at high temperature
(d) ΔH = −ve ΔS = −ve, at low temperature

12. Standard electrode potentials of three metals P, Q and R are –1.3 V, +0.6 V and –4.2 V respectively. Which of the following is correct about their reducing power?
(a) R is weaker reducing agent than Q.
(b) Q is stronger reducing agent than P.
(c) P is weaker reducing agent than R.
(d) R is stronger reducing agent than Q.

13. Assume two radioactive substances A and B disintegrating by
$$\frac{-d[A]}{dt} = k_A[A],\ t_{1/2(A)} = \frac{0.693}{k_A}$$

$$\frac{-d[B]}{dt} = k_B[B]^2,\ t_{1/2(B)} = \frac{1}{k_B[B]_0}$$
If both half-life periods and concentrations are equal, rates at the start of reaction will be in the ratio
(a) 0.693   (b) k_A/k_B
(c) k_B (d) none of these.

14. Which of the following are formed as intermediate products to get naphthalene from benzene and succinic anhydride?

(a)

(b)

(c)

(d)
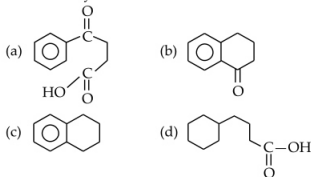
15. A sodium salt on treatment with $MgCl_2$ gives white precipitate only on heating. The anion of the sodium salt is
(a) HCO_3^- (b) CO_3^{2-} (c) NO_3^- (d) SO_4^{2-}

16. Total number of tertiary carbon atoms present in the following compound is
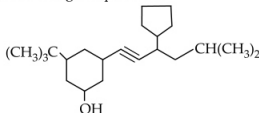
17. A neutral atom of an element has 2 K, 8 L, 9 M and 2 N electrons. Total number of s electrons is

18. The coefficient of H_2S on balancing the equation
$$K_2Cr_2O_7 + H_2SO_4 + H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + S \text{ is}$$

19. For the reaction $A + B \rightarrow C$, it is found that doubling the concentration of A increases the rate by 4 times, and doubling the concentration of B doubles the reaction rate. The overall order of the reaction is

20. van't Hoff factor of an electrolyte X_3Y_2 assuming that it ionizes 25% in the solution is

SECTION-I
One or More Options Correct Type

This section contains 8 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

1. Which of the following compounds give glyoxal as one of the product on ozonolysis?
(a) Benzene
(b) o-Xylene
(c) 2-Methylbut-2-ene
(d) 2, 4-Dimethylhex-1, 3, 5-triene

2. On mixing equal volumes of the following solutions, precipitation of AgCl will occur with (K_{sp} for AgCl is 1.8×10^{-10})
(a) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(b) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)
(c) 10^{-3} M (Ag^+) and 10^{-3} M (Cl^-)
(d) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)

3. Which of the following do not form Grignard's reagent on reaction with Mg in the presence of ether?
(a) $C_6H_5Cl \xrightarrow{Mg/dry\ ether}$
(b) $CH_2 = CH - Cl \xrightarrow{Mg/dry\ ether}$
(c) $CH_2 = CH - CH_2 - Cl \xrightarrow{Mg/dry\ ether}$
(d) $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\!\!\!> CH - Cl \xrightarrow{Mg/dry\ ether}$

4. Select the correct statement(s) if 9.65 ampere current is passed for 1 hour through the cell
$$Ag \mid Ag^+ \mid\mid Cu^{2+} \mid Cu :$$
$$\quad\ \ 1\,M \qquad 1\,M$$
(a) Ag will oxidise to Ag^+ and new $[Ag^+]$ = 1.36 M
(b) Ag^+ will reduce to Ag and new $[Ag^+_1]$ = 0.64 M
(c) Cu^{2+} will reduce to Cu and new $[Cu^{2+}]$ = 0.82 M
(d) Cu will oxidise to Cu^{2+} and new $[Cu^{2+}]$ = 0.82 M

5. Which of the following statement(s) is/are correct?
(a) n/p ratio decreases during α-emission.
(b) n/p ratio increases during β-emission.
(c) α- and β- emissions are secondary emissions and γ-emissions are primary emissions.
(d) If n/p ratio > 1.5 nucleus is unstable.

6. The oxidation states of the most electronegative element in the products of the reaction between BaO_2 with dil. H_2SO_4 are
(a) − 1
(b) + 1
(c) − 2
(d) 0

7.
$$H_3C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{-CH-}}\ \ \xrightarrow{Cl_2,\ h\nu}\ N \text{ (isomeric products) } C_5H_{11}Cl$$
$$\xrightarrow{\text{fractional distillation}} M \text{ (isomeric products)}$$
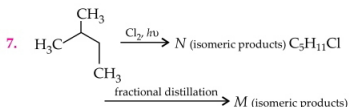
The numbers of N and M are
(a) 6, 6
(b) 6, 4
(c) 4, 4
(d) 3, 3

8. According to Ellingham diagram, the oxidation reaction of carbon to carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature?
(a) Al_2O_3
(b) Cu_2O
(c) MgO
(d) ZnO

SECTION - II
Paragraph Type

This section contains 4 paragraphs each describing theory, experiment, data etc. Eight questions relate to four paragraphs with two questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 9 and 10

There are two kinds of voids that occur in all closest packings. If a triangular void has a sphere over it, there results a void with four spheres around it, called a tetrahedral void. For such a void, four spheres are arranged in the corners of a regular tetrahedron.
If a triangular void pointing up in one close-packed layer is covered by a triangular void pointing down in an adjacent layer, then a void surrounded by six spheres results. These six spheres are arranged at the corners of a regular octahedron and such a void is called an octahedral void.

9. The number of tetrahedral voids in a closest packing is equal to the
(a) number of spheres
(b) thrice the number of spheres
(c) twice the number of octahedral voids
(d) none of these.

10. In a crystalline solid, having formula AB_2O_4, oxide ions are arranged in cubic close packed lattice while cations A are present in tetrahedral voids and cations B are present in octahedral voids. The percentage of the tetrahedral voids occupied by A and the percentage of the octahedral voids occupied by B are respectively
(a) 45.5%, 13.0%
(b) 50%, 12.5%
(c) 13.0%, 45.5%
(d) 12.5%, 50%

The S_N2 reaction occurs in one step, the rate is dependent on both the concentration of substrate and that of the nucleophile (Bimolecular).

The S_N1 reaction proceeds stepwise. The leaving group first leaves, whereupon a carbocation forms that is attacked by the nucleophile. The rate is dependent only on the concentration of substrate (Unimolecular).

In the S_N2 reaction, steric hindrance plays an important role. Since the S_N2 proceeds through a backside attack, the more groups that are present around the vicinity of the leaving group, the slower the reaction will be.

In the S_N1 reaction, carbocation stability plays an important role. Since the first step of the S_N1 reaction is loss of a leaving group to give a carbocation, the rate of the reaction will be proportional to the stability of the carbocation. Carbocation stability increases with increasing substitution of the carbon (tertiary > secondary >> primary) as well as with resonance.

11. Which of the following compounds will undergo an S_N2 reaction most readily?
 (a) $(CH_3)_3CCl$
 (b) $(CH_3)_2CHI$
 (c) $(CH_3)_2CHCH_2CH_2CH_2I$
 (d) $(CH_3)_2CHCH_2CH_2CH_2Cl$

12. Which of the following statements is incorrect?
 (a) S_N2 reaction tends to proceed with strong nucleophiles like negatively charged nucleophiles such as CH_3O^-.
 (b) S_N1 reaction tends to proceed in polar protic solvents such as water.
 (c) S_N1 reaction tends to proceed with weak nucleophiles like neutral compounds such as CH_3OH.
 (d) S_N2 reaction is favoured by polar protic solvents.

Thermodynamic stability of the compounds of transition elements can be evaluated in terms of the magnitude of ionization enthalpies of the metals — smaller the ionization enthalpy of the metal, stabler is its compound.

In solution, the stability of the compounds depends upon electrode potentials rather than ionization enthalpies. Electrode potential values depend upon factors such as enthalpy of sublimation (or atomisation) of the metal, the ionization enthalpy and the hydration enthalpy.

$$\Delta_T H = \Delta_{sub}H + \Delta_i H + \Delta_{hyd}H$$

The electrode potentials are measures of $\Delta_T H$.

13. The observed values of $E°$ and those calculated using the data are compared in the given graph :

Observed values ♦   Calculated values ■
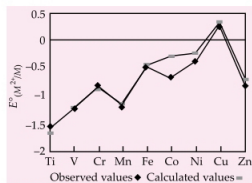
Copper has positive value for reduction potential because of
 (a) high enthalpy of hydration and low enthalpy of atomisation and low enthalpy of ionization.
 (b) low enthalpy of hydration and low enthalpy of atomisation and low enthalpy of ionization.
 (c) high enthalpy of hydration and high enthalpy of atomisation and high enthalpy of ionization.
 (d) low enthalpy of hydration and high enthalpy of atomisation and high enthalpy of ionization.

14. Observe the given data :

Element	Ni	Pt
$(IE_1 + IE_2)$ kJ mol^{-1}	2.49×10^3	2.66×10^3
$(IE_3 + IE_4)$ kJ mol^{-1}	8.80×10^3	6.70×10^3
Total (kJ mol^{-1})	11.29×10^3	9.36×10^3

Identify the correct statement.
 (a) K_2PtCl_6 is a stable compound while K_2NiCl_6 is an unknown compound.
 (b) $NiCl_2$ is a stable compound while $PtCl_2$ is an unstable compound.
 (c) $PtCl_4$ is a stable compound while $NiCl_4$ is an unstable compound.
 (d) All of these are correct.

A scarlet compound (A) is treated with conc. HNO_3 to give a chocolate brown precipitate (B). The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate (C). The precipitate (B) on warming with conc. HNO_3 in the presence of $Mn(NO_3)_2$ produces a pink coloured solution due to the formation of (D).

15. Compound (A) is
 (a) PbO_2 (b) $Pb(NO_3)_2$
 (c) Pb_3O_4 (d) $Pb(MnO_4)_2$

16. Compound (D) is
 (a) Pb_3O_4 (b) $Pb(MnO_4)_2$
 (c) $Pb(NO_3)_2$ (d) PbO_2

CONCEPT MAP

ALCOHOLS, PHENOLS AND ETHERS

Alcohols

Hydroxyl derivatives of aliphatic hydrocarbons
General formula : $C_nH_{2n+1}OH$

Structure

142 pm, 96 pm, 108.9°, H

Classification

C_{sp^3}—OH bond
- 1° : —OH attached to 1°C, —CH_2OH
- 2° : —OH attached to 2°C, $\diagup CH$—OH
- 3° : —OH attached to 3°C, $\diagup C$—OH
- Allylic : $\diagup C$=CH—CH_2—OH
- Benzylic : C_6H_5—CH_2—OH

C_{sp^2}—OH bond
- Vinylic : $\diagup C$=CH—OH
- Arylic : C_6H_5—$OH_{(Phenol)}$

Physical Properties

- B. pt. ∝ No. of C atoms (van der Waals' forces)
- B. pt. ∝ 1/Branching (1° > 2° > 3°)
- B. pt. of alcohols and phenols are higher than that of hydrocarbons, ethers, haloalkanes, haloarenes of comparable molecular masses due to intermolecular H-bonding.
- Solubility ∝ 1/Size of alkyl or aryl groups
- Solubility ∝ Branching (3° > 2° > 1°)
- Soluble in water due to H-bonding.
- Phenols are less soluble than alcohols due to large hydrocarbon part (benzene ring).

Chemical Properties

Cleavage of O—H bond (ease of reaction depends on stability of alkoxide ion or phenoxide ion)
- Alcohols act as nucleophiles.
- Acidity : Phenols > Water > 1° alcohol > 2° alcohol > 3° alcohol
- EWG increases while EDG decreases acidity.

Cleavage of C—OH bond (ease of reaction depends on stability of carbocations)
- Alcohols act as electrophiles.
- Order of reactivity : 3° > 2° > 1°

Reactions involving whole alcohol molecule
- Dehydration :
$$R—OH + conc.\ H_2SO_4 \xrightarrow{443\ K} \diagup C=C\diagdown$$
$$\xrightarrow{413\ K} ROR \xrightarrow{383\ K} RO—SO_2OH$$
$$R—OH + Al_2O_3 \xrightarrow{513\ K} ROR$$
$$\xrightarrow{633\ K} \diagup C=C\diagdown$$

- Oxidation :
Alcohol $\xrightarrow[Cu/573\ K]{[O]}$ Aldehyde/Ketone $\xrightarrow{[O]}$ Carboxylic acid

Preparation

$$\diagup C=C\diagdown \ _{Alkene} \xrightarrow[(Markovnikov's\ rule)]{conc.\ H_2SO_4/H_2O} RCH_2OH$$
(i) B_2H_6 in THF
(ii) H_2O_2, OH^- (Anti-Markovnikov's rule)

$$\begin{array}{c} HCHO \\ or \\ RCHO \\ or \\ R\diagdown C=O \\ R'\diagup \\ Carbonyl\ compounds \end{array} \xrightarrow[Reduction]{} \begin{array}{c} RCH_2OH \\ 1°\ Alcohol \\ or \\ R—CH—R \\ \ \ \ OH \\ 2°\ Alcohol \end{array}$$

H_2/Pt or Pd or Ni or $NaBH_4$ or $LiAlH_4$ or Na/C_2H_5OH

Grignard's reagent (i) $RMgX/Dry$ ether (ii) H_2O/H^+ → R_3C—OH 3° Alcohol

$$RCOOH \ _{Carboxylic\ acids} \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4\ or\ B_2H_6/ether} RCH_2OH$$

Distinction Test

Alcohol	Dichromate (Oxidation) test	Victor Meyer test	Lucas test
1°	Acid (Orange solution becomes green)	Blood red colour	No turbidity
2°	Ketone (Orange solution becomes green)	Blue colour	Turbidity in 5 minutes
3°	No reaction	Colourless	Turbidity immediately

Phenols

Simplest hydroxyl derivative of benzene and its derivatives
General formula : C_6H_5OH

Structure

109°, 136 pm, sp², H

Chemical Properties

Electrophilic substitution of phenols
- Halogenation, sulphonation, nitration, Friedel – Crafts alkylation, etc.
- Occurs at o- and p- positions due to activating effect of —OH group.

Preparation

$$C_6H_5SO_3H \xrightarrow[H_2O]{NaOH} C_6H_5SO_3Na \xrightarrow[-Na_2SO_3-H_2O]{NaOH\ 573-623\ K} C_6H_5ONa \xrightarrow[-NaCl]{dil.\ HCl}$$

$$C_6H_5N_2^+ + H_2O \xrightarrow[-N_2\ -HCl]{623\ K,\ 320\ atm} $$

$$C_6H_5Cl + NaOH \xrightarrow[-NaCl,\ -H_2O]{623\ K,\ 320\ atm} C_6H_5ONa \xrightarrow[-NaCl]{dil.\ HCl}$$

$$C_6H_5CH(CH_3)_2 \xrightarrow[2.\ H^+,\ H_2O]{1.\ O_2}$$
Cumene

→ C_6H_5OH Phenol

Distinction Test

Test	Observation
$FeCl_3$ test	Violet colour
Br_2-H_2O test	White ppt.
Liebermann's nitroso test ($NaNO_2$ + conc. H_2SO_4)	Deep green/blue colour which changes into red on dilution.
Ammonia/Sodium hypochlorite test	Blue colour
Azo dye test	Orange colour

Ethers

Alkoxy or aryloxy derivatives of aliphatic or aromatic hydrocarbons
General formula : $C_nH_{2n+2}O$ (where $n > 1$)

Structure

141 pm, O, 111.7°, sp³

Classification

- Simple or Symmetrical : Same alkyl groups are attached to oxygen, ROR.
- Mixed or Unsymmetrical : Different alkyl groups are attached to oxygen, ROR'.
- Aliphatic Ethers : R and R' both are alkyl groups.
- Aromatic Ethers : Either one or both R and R' are aryl groups.

Preparation

$$2ROH \xrightarrow[or\ Al_2O_3,\ 523\ K]{conc.\ H_2SO_4,\ 413\ K} \boxed{ROR}\ Ether$$

$$RX + RONa \xrightarrow[-NaX]{\Delta}$$
(Williamson synthesis)

- Williamson synthesis involves S_N2 mechanism of an alkoxide ion on 1° alkyl halide.
- In the case of 2° and 3° alkyl halides, elimination takes place.
- Dehydration of alcohols for the formation of ethers follows the order :
1° > 2° > 3°

Chemical Properties

- Reaction of ethereal oxygen
$$ROR + HCl(conc.) \longrightarrow \left[\begin{array}{c} R \\ R \end{array} \diagdown \overset{+}{O}—H \right] Cl^-$$

- Cleavage of C – O bond
$$R—OR + HX \xrightarrow{373\ K} R—OH + R—X$$
In case of alkyl aryl ethers, phenol and an alkyl halide are obtained.
- $ROR + H_2O \xrightarrow[\Delta]{dil.\ H_2SO_4} 2R—OH$
- $ROR + PCl_5 \xrightarrow{\Delta} 2R—Cl$
- Reactions involving alkyl group
  - Formation of peroxides with air and light.
  - Substitution products obtained on halogenation.
- Electrophilic substitution reactions
Aryl alkyl ethers give o- and p-substituted products due to +R effect of alkoxy group (–OR).

Physical Properties

- C – O bonds are slightly polar.
- B. pt. are lower than isomeric alcohols.
- Solubility ∝ 1/Molecular mass (soluble upto three carbon atoms due to H-bonding)
- Fairly soluble in all organic solvents.
- Lighter than water.

Matching List Type

This section contains 4 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

17. Match the list I with list II and select the correct answer using the code given below the lists :

List I	List II
P. $MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$ Eq. wt. of $KMnO_4$ is equal to	1. 36
Q. $H_2O_2 \longrightarrow 2H^+ + O_2$ Eq. wt. of H_2O_2 is equal to	2. 45
R. $Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$ Eq. wt. of $Cr_2O_7^{2-}$ is equal to	3. 31.6
S. $C_2H_2O_4 \longrightarrow 2CO_2 + 2H^+$ Eq. wt. of $C_2H_2O_4$ is equal to	4. 17

	P	Q	R	S
(a)	3	4	2	1
(b)	2	3	4	1
(c)	3	4	1	2
(d)	2	1	3	4

18. Match the reactions given in list I with their types given in list II and select the correct answer using the code given below the lists :

List I	List II
P. $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$	1. Electrophilic addition
Q. $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$	2. Free radical addition
R. $CH_3CH=CH_2 + HBr \longrightarrow CH_3CHBrCH_3$	3. Free radical substitution
S. $CH_3CH=CH_2 \xrightarrow{HBr/Peroxide} CH_3CH_2CH_2Br$	4. Electrophilic substitution

	P	Q	R	S
(a)	1	2	3	4
(b)	3	1	2	4
(c)	4	3	1	2
(d)	3	4	1	2

19. Match the list I with list II and select the correct answer from the code given below the lists :

List I	List II
P. Neutral amino acid	1. Alanine
Q. Acidic amino acid	2. Arginine
R. Isoelectric point, pI = 6.01	3. Aspartic acid
S. Basic amino acid	4. Valine

	P	Q	R	S
(a)	1	2	3	4
(b)	3	2	4	1
(c)	4	3	1	2
(d)	3	4	1	2

20. Match the compounds given in list I with their uses in list II and select the correct answer from the code given below the lists :

List I	List II
P. NaOH	1. Glass
Q. $Na_2S_2O_3$	2. Germicide
R. NaCN	3. Antichlor
S. Na_2CO_3	4. Soap

	P	Q	R	S
(a)	4	3	2	1
(b)	3	4	1	2
(c)	2	3	4	1
(d)	1	2	3	4

SOLUTIONS

PAPER-I

1. (c) :
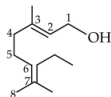
6-Ethyl-3, 7-dimethyloct-2, 6-dien-1-ol

2. (b): $Pt | H_2(1 \text{ atm}) | HA_2 | | HA_1 | H_2(1 \text{ atm}) | Pt$

At anode : $E_{(H^+/H_2)_2} = E°_{(H^+/H_2)_2} + 0.059 \text{ (pH)}_2$

At cathode : $E_{(H^+/H_2)_1} = E°_{(H^+/H_2)_1} + 0.059 \text{ (pH)}_1$ ($\because$ pH = $-\log[H^+]$)

We know, $[H^+] = C\alpha = \sqrt{K_a C}$

$pH_1 = \frac{1}{2}pK_{a_1} - \frac{1}{2}\log C$

$pH_2 = \frac{1}{2}pK_{a_2} - \frac{1}{2}\log C$

$E°_{cell} = E°_{(H^+/H_2)_1} - E°_{(H^+/H_2)_2}$

$= 0.059 \left[\frac{1}{2}pK_{a_2} - \frac{1}{2}pK_{a_1} \right]$

$= \frac{0.059}{2}(5-3) = 0.059 \text{ V}$

3. (c) : $Na[Cr(NH_3)_2(ox)_2] \cdot 3H_2O$.

Coordination number of Cr is 6.

Oxidation number of Cr is +3.

Electronic configuration of Cr^{3+} is $3d^3$

Number of d-electrons in Cr^{3+} is 3.

Number of unpaired d-electrons in Cr^{3+} is 3.

Magnetic moment,

$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$

4. (d): According to MOT, the electronic configuration of

$N_2 : \sigma1s^2, \sigma*1s^2, \sigma2s^2, \sigma*2s^2, \pi2p_x^2 = \pi2p_y^2, \sigma2p_z^2$
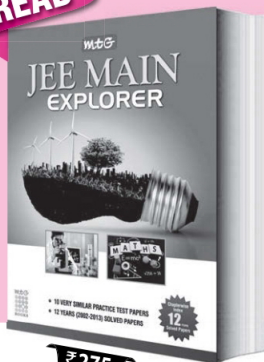
Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$

N_2^+ : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^1$

Bond order $= \frac{1}{2}(9 - 4) = 2.5$

N_2^- : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1$

Bond order $= \frac{1}{2}(10 - 5) = 2.5$

N_2^{2-} : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2,$
$\sigma 2p_z^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$
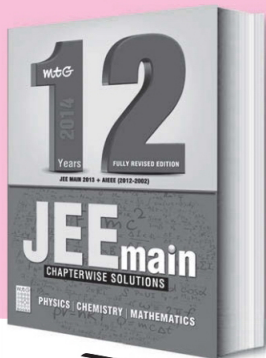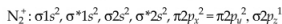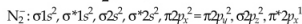
Bond order $= \frac{1}{2}(10 - 6) = 2$

As bond length is inversely proportional to the bond order, their bond lengths will be in the order

$N_2^{2-} > N_2^+ = N_2^- > N_2$
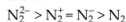
5. **(c)** : Molecular weight of X_2Y_3

$= \frac{32.0 \text{ g}}{0.20 \text{ mol}} = 160 \text{ g mol}^{-1}$

Molecular weight of X_3Y_4

$= \frac{92.8 \text{ g}}{0.4 \text{ mol}} = 232 \text{ g mol}^{-1}$

Let the atomic weight of $X = a$ and atomic weight of $Y = b$.

Then $2a + 3b = 160$ ...(i)
and $3a + 4b = 232$ ...(ii)

Now multiply eq. (i) by (3) and (ii) by (2) we get, $6a + 9b = 480$ ...(iii)
$6a + 8b = 464$ ...(iv)

On subtracting eq. (iv) from (iii) we get,
$b = 16$

On substituting this value in eq. (i) we get,
$2a + 3 \times 16 = 160$
$a = 56$

6. **(b):**

(X)
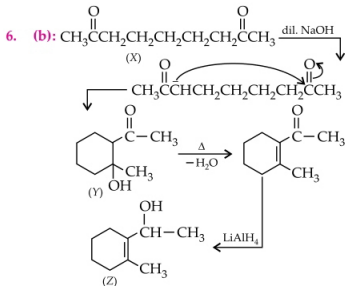
7. **(d):** Hybridisation : $sp^3 \quad sp^2 \quad sp$

% of s character : 25 33 50

∴ The order of increasing s character is

$BF_4^- (sp^3) < BF_3 (sp^2) < BF_2^+ (sp)$
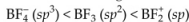
8. **(d):**
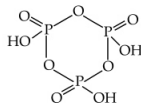
Cyclotrimetaphosphoric acid, $(HPO_3)_3$

9. **(c) :** As in this reaction NH_3 is loosing a proton.

10. **(d):** NaCl has a face-centred cubic close packing in which lattice points are occupied by Cl^- ions whereas Na^+ ions occupy all octahedral holes. Here Na^+ and Cl^- both have a coordination number of 6.

(i) Effective no. of A^- or Cl^- (normally)

$= \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$ (∵ from corners and face centres)

Effective no. of A^- after removing atoms along one axis

$= \left(8 \times \frac{1}{8}\right) + \left(4 \times \frac{1}{2}\right) = 3$

(ii) Effective no. of B^+ or Na^+

$= \left(12 \times \frac{1}{4}\right) + 1 = 4$ (∵ from edge centres and body centre)

∴ Formula is A_3B_4.

11. **(b,d) :** $\Delta H = +ve$, $\Delta S = +ve$, if $\Delta H < T\Delta S$ then $\Delta G < 0$ *i.e.* at high temperature, reaction will be spontaneous.

$\Delta H = -ve$, $\Delta S = -ve$, if $\Delta H > T\Delta S$, then $\Delta G < 0$ *i.e.* at low temperature, reaction will be spontaneous.

12. **(c,d)** : More negative the standard electrode potential value, stronger is the reducing agent.

$R > P > Q$

13. **(a):** $t_{1/2(A)} = t_{1/2(B)}$

$\frac{0.693}{k_A} = \frac{1}{k_B [B]_0}$

$\frac{k_A}{k_B} = 0.693 [B]_0 = 0.693 [A]_0$

Rate, $r_A = k_A [A]_0$

$r_B = k_B [B]_0^2 = k_B [A]_0^2$

$\frac{r_A}{r_B} = \frac{k_A}{k_B [A]_0} = 0.693$

14. (a,b,c) :

15. (a) : $MgCl_2 + 2NaHCO_3 \rightarrow \underset{\text{Soluble}}{Mg(HCO_3)_2} + 2NaCl$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{(white ppt.)}}{MgCO_3 \downarrow} + H_2O + CO_2$$

16. (5) :
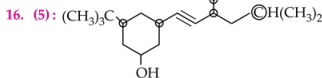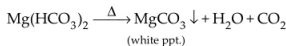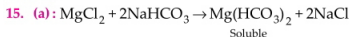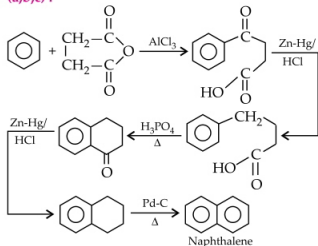
Encircled carbon atoms in this compound are tertiary carbon atoms (carbon atoms directly attached to three other carbon atoms).

17. (8) : The electronic configuration of neutral atom is

$$\underset{K}{1s^2} \quad \underset{L}{2s^2 \ 2p^6} \quad \underset{M}{3s^2 \ 3p^6 \ 3d^1} \quad \underset{N}{4s^2}$$

18. (3) : $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4$
$\qquad\qquad + Cr_2(SO_4)_3 + 7H_2O + 3S$

19. (3) : $A + B \longrightarrow C$
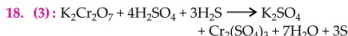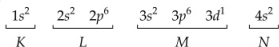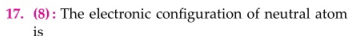
On doubling the concentration of A, rate of reaction increases by 4.

$$Rate \propto [A]^2$$

However, on doubling the concentration of B, rate of reaction increases two times.

$$Rate \propto [B]$$

Thus, overall order of reaction $= 2 + 1 = 3$

20. (2) :

	X_3Y_2	$\rightleftharpoons$	$3X^{2+}$	$+$	$2Y^{3-}$
Initial conc.	1 mol		0		0
After ionization	1 − 0.25		3 × 0.25		2 × 0.25
	0.75		0.75		0.5
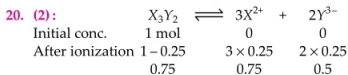
Total number of moles after dissociation
$$= 0.75 + 0.75 + 0.5 = 2$$
$\therefore \ i = 2$

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1. (a,b) :
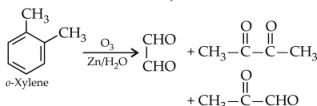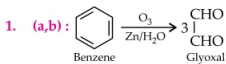
2. (c,d) : Precipitation occurs when
ionic product > solubility product
(c) ionic product $= 10^{-3} \times 10^{-3} = 10^{-6}$
$\therefore \ K_{ip} > K_{sp}$
(d) $K_{ip} = 10^{-4} \times 10^{-4} = 10^{-8}$
$\qquad K_{ip} > K_{sp}$
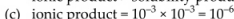
3. (a,b) : Cl atom attached to sp^2 hybridized C-atom have some double bond character between C – Cl bond due to resonance hence difficult to cleave.

4. (a,c) : $\dfrac{w}{E} = \dfrac{It}{96500} = \dfrac{9.65 \times 3600}{96500}$
$\qquad\qquad = 0.36$ eq. of $Ag^+ = 0.36$ eq. of Cu^{2+}
$\qquad\qquad = 0.36$ mole of $Ag^+ = 0.18$ mole of Cu^{2+}
Now, Ag will oxidise to Ag^+ and Cu^{2+} will reduce to Cu.
And new $[Ag^+] = 1 + 0.36 = 1.36$ M
$\qquad$ new $[Cu^{2+}] = 1 - 0.18 = 0.82$ M

5. (d)
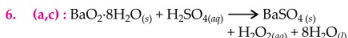
6. (a,c) : $BaO_2 \cdot 8H_2O_{(s)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4\,(s)}$
$\qquad\qquad\qquad\qquad\qquad + H_2O_{2(aq)} + 8H_2O_{(l)}$
Most electronegative element in products is oxygen. In H_2O_2 oxidation state of O is – 1 and in $BaSO_4$, –2.

7. (b) :
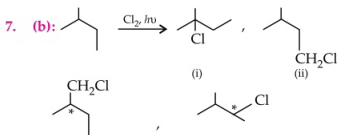
Total 6 isomers will be formed out of which only 4 isomers will be obtained on fractional distillation as ($d + l$) mixture will not be separated by distillation.
Methods used for separation of optically active compounds are chromatography, mechanical separation, biochemical separation, chemical separation, etc.

8. (b): In the graph of $\Delta_r G°$ vs T for formation of oxides, the Cu_2O line is almost at the top. So, it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower temperature (500 - 600 K)).

$$Cu_2O + C \longrightarrow 2Cu + CO$$

9. (c): The number of octahedral voids in a closest packing is equal to the number of spheres and the number of tetrahedral voids in a closest packing is twice the number of spheres or twice the number of octahedral voids.

10. (d): In a cubic close packed lattice of oxide ions there would be two tetrahedral voids and one octahedral void for each oxide ion.

∴ For four oxide ions there would be 8 tetrahedral and 4 octahedral voids.

Percentage of tetrahedral voids occupied by

$$A = \frac{1}{8} \times 100 = 12.5\%$$

Percentage of octahedral voids occupied by

$$B = \frac{2}{4} \times 100 = 50\%$$

11. (c): Since steric hindrance increases as we go from primary to secondary to tertiary, the rate of S_N2 reaction proceeds from primary (fastest) > secondary > tertiary (slowest). I^- is a better leaving group than Cl^- as less bond dissociation energy is required to break C — I bond as compared to C — Cl bond.

12. (d): S_N2 reaction is favoured by polar aprotic solvents such as acetone, DMSO, acetonitrile or DMF etc.

13. (d): The reason for positive $E°$ value for copper is that the sum of high enthalpies of atomisation and ionization is not balanced by low hydration enthalpy.

14. (d)

15. (c): The scarlet red compound (A) is Pb_3O_4.

$$\underset{(A)}{Pb_3O_4} + 4HNO_{3(conc.)} \longrightarrow$$
$$\underset{\text{Solution}}{2Pb(NO_3)_2} + \underset{\substack{\text{Brown ppt.}\\(B)}}{PbO_2\downarrow} + 2H_2O$$

$$Pb(NO_3)_2 + 2KI \longrightarrow \underset{\substack{\text{Yellow ppt.}\\(C)}}{PbI_2\downarrow} + 2KNO_3$$

16. (b): $5PbO_2 + \underset{(B)}{2Mn(NO_3)_2} + 4HNO_3 \longrightarrow 4Pb(NO_3)_2$
$$+ \underset{\substack{\text{Purple colour}\\(D)}}{Pb(MnO_4)_2} + 2H_2O$$

17. (c): P. $\overset{+7}{Mn}O_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
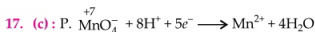
Total number of electrons gained = 5

$$\text{Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{5}$$
$$= \frac{39 + 55 + 4 \times 16}{5} = \frac{158}{5} = 31.6$$

Q. $\overset{-1}{H_2}O_2 \longrightarrow 2H^+ + \overset{0}{O_2} + 2e^-$
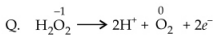
Total number of electrons lost = 2

$$\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt. of } H_2O_2}{2}$$
$$= \frac{2 + 32}{2} = \frac{34}{2} = 17$$

R. $\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$
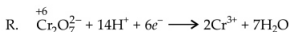
Total number of electrons gained = 6

$$\text{Eq. wt. of } Cr_2O_7^{2-} = \frac{\text{Mol. wt. of } Cr_2O_7^{2-}}{6}$$
$$= \frac{2 \times 52 + 7 \times 16}{6} = \frac{216}{6} = 36$$

S. $\underset{\text{Oxalic acid}}{\overset{+3}{C_2}H_2O_4} \longrightarrow 2\overset{+4}{C}O_2 + 2H^+ + 2e^-$
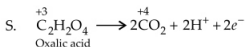
Total number of electrons lost = 2

$$\text{Eq. wt. of } C_2H_2O_4 = \frac{\text{Mol. wt. of } C_2H_2O_4}{2}$$
$$= \frac{24 + 2 + 64}{2} = \frac{90}{2} = 45$$

18. (d)

19. (c):
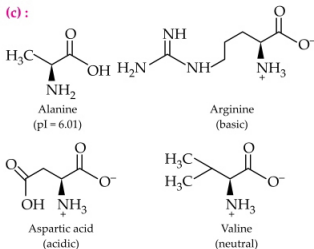
Alanine
(pI = 6.01)

Arginine
(basic)

Aspartic acid
(acidic)

Valine
(neutral)

20. (a)

LEARN FAST

Coordination Compounds

Addition Compounds

Addition compound is formed, when a solution containing two or more simple stable compounds is allowed to stand.

- ❑ Addition compounds, also called molecular compounds are grouped into two categories:
  - ○ **Double salts :** These are formed by mixing two apparently saturated compounds which lose their identity when dissolved in water or melted to complete ionization. These are also called lattice compounds.
    - – They give test for all individual ions.
    - – They exist only in the solid state.

    $$KCl.MgCl_2.6H_2O \longrightarrow K^+ + Mg^{2+} + 3Cl^- + 6H_2O$$
    Carnallite
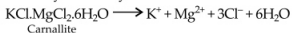
  - ○ **Complex or coordination compounds :** These are the compounds in which the central metal atom is linked to number of ions or neutral molecules by coordinate bonds (*i.e.*, donation of electron pairs).
    - – Some of the constituent ions or molecules lose their identity when dissolved in water due to formation of complex ion.
    - – They do not give test for all constituent ions.
    - – They exist in solid state as well as in aqueous solution.

    $$[Cu(NH_3)_4]SO_4 \longrightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$
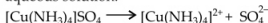
Terminology of Coordination Compounds

- ❑ **Central metal atom/ion :** Central metal atom/ion to which one or more neutral molecules or ions are linked by coordinate bonds in a definite geometrical arrangement around it. It is also referred as Lewis acid.
- ❑ **Ligand :** An atom, molecule or ion which is linked to central metal atom/ion through coordinate bond by donating lone pair of electrons present on its donor atom.
- ❑ **Types of Ligands**
  - ○ **On the basis of charge**
    - – Negative ligand which carries negative charge. *e.g.*, CN^-

- – Positive ligand which carries positive charge. *e.g.*, NO_2^+
- – Neutral ligand which does not carry any charge, *e.g.*, H_2O

- ○ **On the basis of number of donor sites**
  - – Monodentate or unidentate ligand which coordinates to central metal atom/ion through one donor atom and forms only one coordinate bond *e.g.*, NH_3, OH^-
  - – Bidentate ligand which coordinates to central metal atom/ion through two donor atoms and forms two coordinate bonds *e.g.*,

    $$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \quad , \overset{..}{N}H_2-CH_2-CH_2-\overset{..}{N}H_2$$
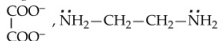
  - – Polydentate ligand which coordinates to central metal atom/ion through more than two donor atoms *e.g.*, EDTA is a hexadentate ligand.

- ○ **On the basis of bonding**
  - – Chelating ligand is a bidentate or polydentate ligand which forms two or more coordinate bonds with central metal atom/ion in such a way that a five or six membered ring is formed.

    Chelating ligand   Chelate
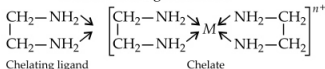
  - – Ambidentate ligand is a monodentate ligand containing more than one coordinating atoms.

    Nitro   Nitrito
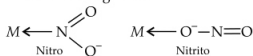
  - – π-acid or π-acceptor or π-bonding ligands are ligands which not only donate their lone pair of electrons to metal atom to form normal σ-bond but also accept an appreciable amount of electron density from filled metal orbital to their vacant π or π* orbitals to form π-bond *e.g.* CO, NO

- **Coordination number :** It is the total number of coordinate bonds through which the central metal atom/ion is attached with ligands or the total number of ligand donor atoms to which the metal is directly bonded. *e.g.*, In $[Cr(H_2O)_6]^{3+}$, coordination number of $Cr = 6$

- **Coordination entity/Coordination sphere :** The central metal atom/ion and the ligands which are directly attached to it are collectively known as coordination sphere. It is non-ionizable and written enclosed in square brackets.

- **Counter ions :** These are the ionizable groups written outside the brackets.

- **Coordination polyhedron :** It is the spatial arrangement of the ligands around the central metal atom/ion.

- **Oxidation number of central metal atom/ion :** It is the number that represents an electric charge which an atom/ion actually have.

- **Charge on complex ion :** The algebraic sum of the charges carried by central metal atom/ion and the ligands coordinated to it. *e.g.*, In $[Ag(CN)_2]^-$, Ag^+ has + 1 charge, CN^- has − 1, net charge $= + 1 − 2 = − 1$.

- **Homoleptic complex** in which metal atom/ion is bound to only one kind of ligands.

- **Heteroleptic complex** in which metal atom/ion is bound to more than one kind of ligands.
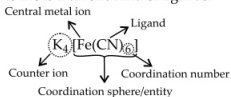
Oxidation number of Fe = + 2

Charge on complex ion = − 4

- **EAN :** It is defined as the total number of electrons on the metal atom/ion after gaining electrons from the donor atoms of the ligands.

  EAN = Atomic no. of metal – No. of electrons lost in ion formation + No. of electrons gained from the donor atoms of the ligands

Nomenclature of Coordination Compounds

- **Rules for naming coordination compounds :**
  - The cation is named first then the anion.
  - In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
  - Name of coordination compounds is started with a small letter and the complex part is written as one word.

- **Naming of ligands :**
  - Name of anionic ligands end in –*o*. *e.g.*, Cl^- : Chlorido
  - Neutral ligands (with a few exceptions) retain their name *e.g.*, NH_3 : Ammine
  - Name of cationic ligands end in – *ium*. *e.g.*, NO_2^+ : Nitronium
  - Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. *e.g.*, ethylenediamine(*en*).
  - Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom. *e.g.*,
    —SCN⁻ : Thiocyanato-S or Thiocyanato
    —NCS⁻ : Thiocyanato-N or Isothiocyanato
    —ONO⁻ : Nitrito-O or Nitrito
    —NO₂⁻ : Nitrito-N or Nitro

- The prefixes *di-, tri-, tetra-, penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis-*(2), *tris-*(3), *tetrakis-*(4), *pentakis-*(5) and *hexakis-*(6).

- When the coordination sphere is anionic, name of central metal ends in –*ate*.

- **Rules for writing the formula of coordination compounds :**
  - Formula of the cation whether simple or complex must be written first followed by anion.
  - The coordination sphere is written in square brackets.
  - Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
  - Polyatomic ligands are enclosed in parentheses.
  - The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.

Isomerism in Coordination Compounds

- Isomers are the compounds with the same molecular formula but different arrangements of atoms. They have different properties.

- They exhibit two types of isomerisms, structural and stereoisomerism.

Structural isomerism
Coordination compounds having different ligands within their coordination spheres.

Ionisation isomerism	**Hydrate/Solvate isomerism**	**Linkage isomerism**	**Coordination isomerism**
Complexes that give different ions in solution. $e.g.,$[Co(NH$_3$)$_5$Br]SO$_4$ [Co(NH$_3$)$_5$SO$_4$]Br	Complexes that differ in number of water molecules present as ligands (inside the coordination sphere) and as free molecules (outside the coordination sphere). $e.g.,$[Cr(H$_2$O)$_6$]Cl$_3$, [Cr(H$_2$O)$_5$Cl]Cl$_2$.H$_2$O	Complexes that differ in the atom of a ligand directly bonded to the metal atom, shown by complexes containing ambidentate ligands. $e.g.,$[Co(NH$_3$)$_5$(NO$_2$)]Cl$_2$ [Co(NH$_3$)$_5$(ONO)]Cl$_2$	Occurs when both positive and negative ions are complex ions and two isomers differ in ligand's distribution in two complex ions. $e.g.,$[Co(NH$_3$)$_6$][Cr(CN)$_6$] [Cr(NH$_3$)$_6$][Co(CN)$_6$]
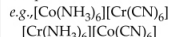
Stereoisomerism
Coordination compounds having different positions and arragements of ligands in space.

Geometrical isomerism
Arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

Optical isomerism
Occurs when a complex is represented by two different structures which are non-superimposable mirror images of each other called enantiomers.

In octahedral complex [Ma_3b_3]
Facial (*fac*) : 3 donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face.
Meridional (*mer*) : When the positions are around the meridian of the octahedron.
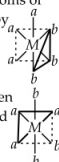
In octahedral complex [Ma_4b_2]

cis   *trans*
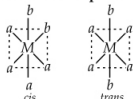
In octahedral complex [$M(aa)_2b_2$] or [$M(aa)_2bc$]

cis   *trans*
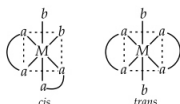
In square planar complex [Ma_2b_2]
cis : 2 same ligands are arranged adjacent to each other.
trans : 2 same ligands are arranged opposite to each other.
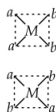
In square planar complex [Ma_2bc]

cis   *trans*
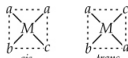
In square planar complex [$Mabcd$]
These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a).

Optical isomerism in [$M(aa)_2b_2$]
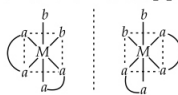
[$M(aa)_3$]
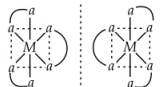
[$M(aa)b_2c_2$]
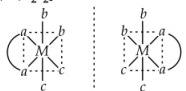
dextro (*d*): Rotates plane of polarised light to right.
laevo (*l*) : Rotates plane of polarised light to left.

Bonding in Coordination Compounds

❑ **Werner's coordination theory :** The main postulates are :

○ Metals possess two types of valencies : primary or principal or ionizable valency and secondary or non-ionizable valency.
  – Primary valency corresponds to the oxidation state of the central metal atom/ion and it is satisfied by negative ions.
  – Secondary valency corresponds to the coordination number of the central metal atom/ion and it is satisfied by neutral molecules or negative ions (ligands) and is fixed for a metal.

○ Every metal atom tends to satisfy both its primary and secondary valencies.

○ Primary valencies are non-directional whereas ligands satisfying secondary valencies are always directed towards fixed positions in space, giving a definite geometry to the complex.

○ On the basis of experimental evidences like number of ions that could be precipitated out and conductivity measurements, he represented primary valencies (ionizable) by dotted lines and secondary valencies (non-ionizable) by solid lines.

$[Co(NH_3)_6]Cl_3$
(Three ionizable chlorine)
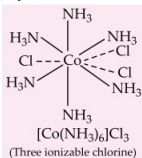
○ Complex with central metal having coordination number 6, shows octahedral geometry. Complex with central metal having coordination number 4, shows either tetrahedral or square planar geometry.

❑ **Valence bond theory (VBT) :** According to this theory, the metal atom/ion makes available empty orbitals equal to its coordination number.

○ The orbitals may be inner orbitals *i.e.*, $(n-1)d$, ns and np or outer orbitals *i.e.*, nd, ns and np depending upon the strength of ligand.

○ The vacant orbitals undergo hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar.

○ These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination number	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where $X = Cl^-$, Br^-, I^-
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$
5	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
6	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Inner orbital complexes	Outer orbital complexes
Involves inner d-orbitals *i.e.* $(n-1)d$-orbitals.	Involves outer d-orbitals *i.e.* nd-orbitals
Low spin complexes	High spin complexes
Have less or no unpaired electrons. *e.g.*, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. *e.g.*, $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

❑ **Magnetic properties**

○ Low spin complexes are diamagnetic (generally).

○ High spin complexes are paramagnetic.

○ Paramagnetism ∝ No. of unpaired electrons

○ Magnetic moment $= \sqrt{n(n+2)}$ B.M.
  (where n = number of unpaired electrons)

❑ **Crystal field theory :** CFT considers the bond to be ionic and the interaction between metal ion and ligands is purely electrostatic.

- Due to their different electrostatic repulsion with the ligands, d-orbitals split into two groups which have different energies. The $d_{x^2-y^2}$ and d_{z^2} orbitals belong to the e_g symmetry group in the octahedral field and the d_{xy}, d_{xz}, and d_{yz} orbitals belong to the t_{2g} symmetry group.

- The energy difference between the two sets of the d-orbitals in the crystal field is known as the ligand field splitting parameter, Δ_o, where the subscript o refers to the fact that it is an octahedral field. Conservation of energy states that the energies of the t_{2g} orbitals lie at $-0.4\Delta_o$ and the e_g orbitals lie at $+0.6\Delta_o$, so the total energy is
$$[3 \times (-0.4\Delta_o)] + [2 \times (+0.6\Delta_o)] = 0$$

Splitting of d-orbitals in an octahedral crystal field
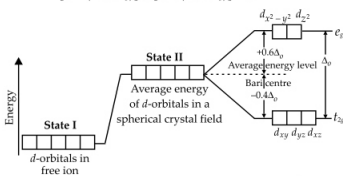
- For tetrahedral crystal field, the order of splitting is reversed and is related to Δ_o as
$$\Delta_t = \frac{4}{9}\Delta_o$$

- The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which the splitting will be large whereas other ligands produce weak fields which result in small splitting of d-orbitals.

- Ligands are arranged in the order of increasing field strength called spectrochemical series.
$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$$

Weak field ligand | Increasing order of CFSE | Strong field ligand
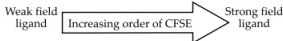
- **Calculation of CFSE for octahedral complexes :**
CFSE $= (-0.4\, x + 0.6\, y)\,\Delta_o$
where,
x = Number of electrons occupying t_{2g} orbitals.
y = Number of electrons occupying e_g orbitals.
  - For complexes in a ligand field, d-orbital occupancy depends on Δ_o and pairing energy, P.

- If $\Delta_o > P$ (i.e. Δ_o large, strong field ligand) → electrons pair-up in lower energy d-subshell first → forms low spin complex.

- If $\Delta_o < P$ (i.e., Δ_o small, weak field ligand) → electrons spread out among all d-orbitals before pairing up → forms high spin complex.

Stability of Coordination Compounds

- It depends on
  - **Charge on the central metal ion (oxidation state) :** Greater the charge on central metal ion, more is the stability.
  - **Basic nature of ligand :** More the basic strength of ligand, more is the stability of complex.
  - **Presence of chelate rings :** Formation of chelate ring increases the stability of complex.
  - **Size of the metal ion :** Smaller the size of metal ion, more is the stability.
  - **Electronegativity and polarising power of the central metal ion :** More is the electronegativity and polarising power of the metal ion, more stable is the complex.

Colour of Coordination Compounds

- The magnitude of CFSE (Δ_o) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever d-d transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.

Applications of Coordination Compounds

- Coordination compounds are of great importance in biological system. e.g. chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordinate compounds of Mg, Fe and Co respectively.

- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.

- cis-platin is used in cancer treatment.

- EDTA is often used for treatment of lead poisoning.

- Coordination compounds are used as catalyst.

Organometallics

❑ These are the compounds which contain one or more metal–carbon bonds.

❑ These are the compounds of metalloids like B, Si, Ge, etc. with organic group.

❑ **Types of organometallic compounds**
Based on the nature of metal-carbon bond, they are classified into three types :

○ **σ-bonded organometallic compounds :** These are formed by main group (s- and p-block) elements, non-metallic and metalloid elements and Zn, Cd, Hg through a normal 2 electron covalent bond. Examples are :

$$R-Mg-X, (C_2H_5)_2Zn \text{ etc.}$$
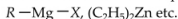
○ **π-bonded organometallic compounds (π complexes) :** These are formed mainly by transition elements. Here normal σ-bond is formed through the π-cloud of electrons of the organic molecule.
Examples are: Zeise's salt, $K[PtCl_3(\eta^2-C_2H_4)]$; ferrocene, $[Fe(\eta^5-C_5H_5)_2]$ etc.

○ **σ- and π- bonded organometallic compounds (Metal carbonyls) :** Transition metal carbonyls constitute this class of organometallics. Examples are homoleptic carbonyls (compounds containing carbonyl ligands only) $[M(CO)_6]$ where M = V, Cr, Mo, W; e.g. $[Fe(CO)_5]$, $[Ni(CO)_4]$

❑ **Bonding in metal carbonyls**
Metal–carbon bond in metal carbonyls possesses both σ- and π-character. Its formation involves following steps :

○ There is an overlap of filled π2p orbital of CO with suitable empty metal orbital resulting in the formation of sigma bond.

Vacant metal orbital   Orbital containing lone pair

$M \leftarrow$ C σ-bond
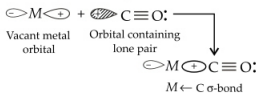
○ Then there is a π-overlap involving filled metal d-orbital and empty antibonding π*2p orbital of same CO. This results in formation of $M \rightarrow$ C π-bond. This is also called back bonding.
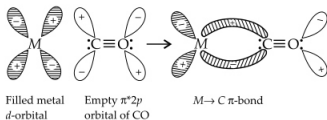
Filled metal d-orbital   Empty π*2p orbital of CO $M \rightarrow$ C π-bond
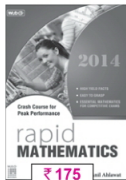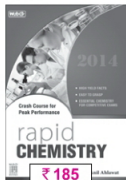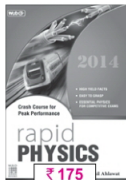
COMPETITION CORNER

Organic Chemistry

Mukul C. Ray, Odisha

Questions from carbohydrates are always observed. This class of compounds is somehow linked to us in our day-to-day life as well. This article is uniquely designed, which combines facts, structures, reactions and information on carbohydrate chemistry.

Nature makes an abundance of compounds with general formula $C_x(H_2O)_y$ in which x and y are whole numbers. These compounds are variously known as sugars, carbohydrates and mono, di or polysaccharides. They are the most abundant class of organic compounds found in living organisms.

On the basis of function, they are classified as:

○ **Aldose :** Sugars having an aldehyde function or an acetal equivalent.

○ **Ketose :** Sugars having a ketone function or an acetal equivalent.

Carbohydrates are produced during the process of photosynthesis, in which energy from the sun is converted into chemical energy by combining CO_2 with H_2O to form carbohydrates and molecular oxygen. Thus, light energy is stored as chemical energy in the form of carbohydrates in plants.

The energy stored in carbohydrates is harvested by non-photosynthesizing organisms in the process known as glycolysis and respiration.

Do you Know?

Current geochemical theory suggests that molecular oxygen was in very low concentration in the atmosphere of the ancient earth and carbohydrates were broken down by the process of anaerobic glycolysis.

$$C_6H_{12}O_6 \xrightarrow[\text{glycolysis}]{\text{Anaerobic}} 2CH_3-\underset{\underset{\text{OH}}{|}}{CH}-COOH + \underset{\text{(2 ATP)}}{\text{Energy}}$$

L-Lactic acid
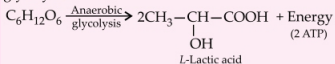
Only a limited amount of energy was available for living organisms via anaerobic glycolysis (2 ATP per $C_6H_{12}O_6$) and life remained simple and primitive. As the concentration of oxygen increased, the mechanism of oxidation changed, which gave much greater amounts of energy (38 ATP per $C_6H_{12}O_6$). This increase in available energy led to an explosion in the number and complexity of organisms.

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{Respiration}} 6CO_2 + 6H_2O + \underset{\text{(38 ATP)}}{\text{Energy}}$$
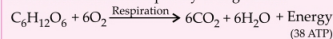
Occurrence of Carbohydrates

○ **Cellulose :** Cellulose is generally related to trees and wood, although this is a relatively impure form of cellulose mixed with many other components such as hemicellulose and lignin.

○ **Starch :** Found in leaves, stems, roots and tubers of plants.

○ **Chitin :** It is related to cellulose in structure. It makes up the major organic component of the exoskeletons of arthropods such as insects, crabs, etc.

○ **Sucrose :** Chiefly found in sugarcane, sugar beet, fruits, etc.

○ ***D*-Glucitol :** Found in fruits, berries such as apples, apricots, cherries and pears.

○ ***D*-Mannitol :** Found in plant exudates and seaweeds.

○ **Xylitol :** The unusual sweet taste of three fruits strawberries, raspberries and plums is due to xylitol.

Remembering the Structure

The trick is not to 'memorise' but to learn the structures by developing a 'system'.

First of all remember the structure of *D*-glucose because it constitutes 99.95% of carbohydrates on earth.

CHO
H——OH
HO——H
H——OH
H——OH
CH₂OH
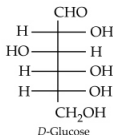
D-Glucose

- Three related compounds are :
  Mannose : C-2 epimer of D-glucose
  Allose   : C-3 epimer of D-glucose
  Galactose : C-4 epimer of D-glucose
- Epimers are the stereoisomers, which differ from each other with respect to configuration at one carbon only.

D-Mannose (Fischer projection: CHO; HO—H; HO—H; H—OH; H—OH; CH$_2$OH)

D-Allose (Fischer projection: CHO; H—OH; H—OH; H—OH; H—OH; CH$_2$OH)
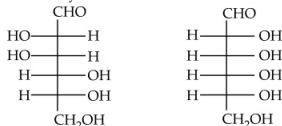
- In pentose sugar category, D-ribose is to be memorised.

D-Ribose (Fischer projection: CHO; H—OH; H—OH; H—OH; CH$_2$OH)
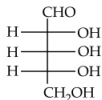
- D/L-Nomenclature is based on two arbitrarily chosen reference compounds.

D-Glyceraldehyde (CHO; H—OH; CH$_2$OH)

L-Glyceraldehyde (CHO; HO—H; CH$_2$OH)
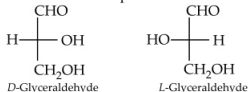
- In the ketose sugar category, just remember D-fructose.

D-Fructose (CH$_2$OH; C=O; HO—H; H—OH; H—OH; CH$_2$OH)
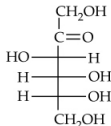
- Xylitol is a sweet miracle.

Xylitol (CH$_2$OH; H—C—OH; HO—C—H; H—C—OH; CH$_2$OH)
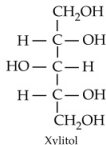
It helps to prevent tooth decay. It reduces plaque formation on teeth. It rates 7 on the glycemic index, a ranking based on immediate effect on blood glucose levels. The glycemic index rates food on a scale of 1-100; foods with the lowest numbers are healthiest. Table sugar or sucrose rates a 65 and glucose a 100.

Ring Structure

Failure of glucose to form bisulphite addition product and an aldehyde-ammonia compound indicates that glucose exists as a ring structure. In addition, though glucose reacts with hydroxylamine but glucose pentaacetate does not form oxime.

To draw the ring structure, fold the open chain structure as shown, so that the groups on the right hand side of Fischer projection are placed below.

(Holding C_4-C_5 bond constant, do the rotation)

D-Glucopyranose
(Haworth Projection)
– OH above, β-anomer
– OH below, α-anomer
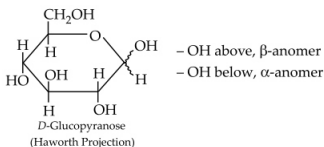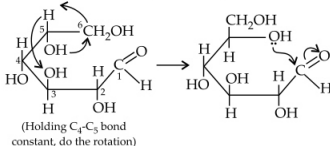
(Note that ⌁ is the undefined stereo bond. It may be up-stereo/down-stereo bond.)

Alternatively,

'O' atom at foot rest

Chair conformation
– OH equatorial, β-anomer
– OH axial, α-anomer
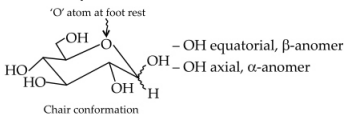
The —CHO function becomes – CH(OH), a new asymmetric carbon, called anomeric carbon.

α-D-Glucopyranose
(Fischer projection)
(H—C—OH; H—OH; HO—H; H—OH; H; CH$_2$OH with O bridge)

β-D-Glucopyranose
(Fischer projection)
(HO—C—H; H—OH; HO—H; H—OH; H; CH$_2$OH with O bridge)
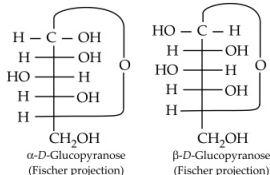
○ Similarly, the five-membered ring structure of *D*-fructose is

D-Fructofuranose

– OH above, β-anomer
– OH below, α-anomer
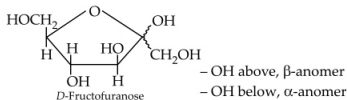
○ Sucrose is a disaccharide made up of *D*-glucose and *D*-fructose having α,β- (1 → 2) glycosidic linkage.

To build the structure, flip the structure to bring anomeric C to the left

Anomeric C on right

Anomeric C on left

β-*D*-Fructofuranose   β-*D*-Fructofuranose

and then join α-*D*-glucose and β-*D*-fructose
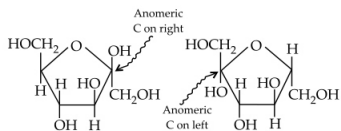
α,β-(1 → 2) linkage
Sucrose
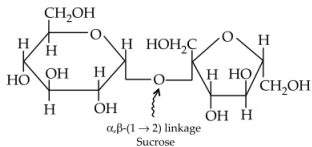
One alternative drawing is, first flip the structure of α-*D*-glucopyranose up-right-down

α-*D*-Glucopyranose   α-*D*-Glucopyranose
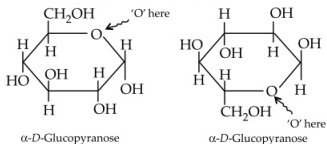
and then join the two

Sucrose
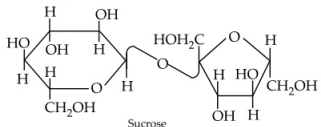
○ The other three disaccharides include cellobiose, maltose and lactose. These contain (1 → 4) glycosidic linkage.

Cellobiose [β-*D*-glucose + β–*D*-glucose, glycosidic linkage (1 → 4)]

Cellobiose
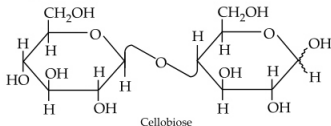
It is all about drawings.; one alternative drawing is

Cellobiose
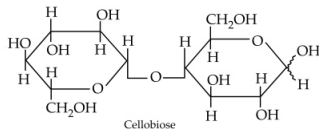
In the Fischer form, it is written as

Cellobiose
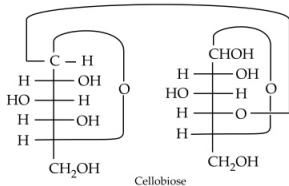
Similarly, all that has to be remembered, is the linkages.

○ **Maltose :** α-*D*-glucose + α-*D*-glucose ; 1 → 4 glycosidic linkage
(called as 4-O-α-*D*-glucopyranosyl-*D*-glucose)

○ **Lactose :** β-*D*-galactose + β-*D*-glucose ; 1 → 4 glycosidic linkage
(called as 4-O-β-*D*-galactopyranosyl-*D*-glucose)

Reactions

○ Some of the very common reactions of glucose are :

○ Other rarely observed reactions include :

$$\text{conc. HNO}_3 \rightarrow CH_3-CO-CH_2-CH_2-COOH$$
Laevulinic acid

$$\text{CHO} \atop (\text{CHOH})_4 \atop \text{CH}_2\text{OH}$$

$$\text{conc. H}_2\text{SO}_4 \rightarrow$$

$$HOCH_2 \overset{O}{\diagup} CHO$$
5-Hydroxymethylfurfural

CH(OH)CN
|
(CHOH)₄
|
CH₂OH
D-Glucose cyanohydrin
(Two isomers)

HCN

CHO
|
(CHOH)₄
|
CH₂OH
D-Glucose

[O]
Br₂–H₂O

COOH
|
(CHOH)₄
|
CH₂OH
Gluconic acid

dil. HNO₃

COOH
|
(CHOH)₄
|
COOH
Glucaric acid/Saccharic acid

HI
heat

$CH_3-(CH_2)_4-CH_3$
n-Hexane

NaBH₄

CH₂OH
|
(CHOH)₄
|
CH₂OH
D-Glucitol/Sorbitol

○ Malaprade oxidation is done by using HIO₄.

CHO
CHOH
CHOH
CHOH
CHOH
CH₂OH

$\xrightarrow{5\text{HIO}_4}$ 5HCOOH + HCHO
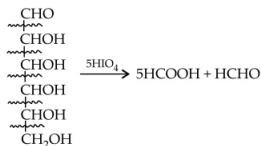
○ With PhNHNH₂, *D*-glucose undergoes condensation reaction.

CH=O
|
CHOH
|
(CHOH)₃
|
CH₂OH

$\xrightarrow[-H_2O]{PhNHNH_2}$

CH=NNHPh
|
CHOH
|
(CHOH)₃
|
CH₂OH

$\xrightarrow[-PhNH_2, -NH_3]{PhNHNH_2}$

CH=NNHPh
|
C=NNHPh
|
(CHOH)₃
|
CH₂OH
Osazone

$\xleftarrow{PhNHNH_2}$

CH=NNHPh
|
C=O
|
(CHOH)₃
|
CH₂OH

○ A very important conceptual reaction is :

$$\xrightarrow[\text{gas}]{CH_3OH \atop \text{dry HCl}}$$
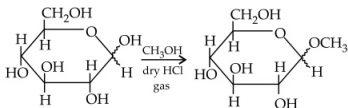
This reaction passes through a carbocation, stabilised with the help of lone pair on oxygen.
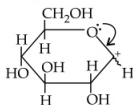
○ Some of the reactions of fructose include :

CH₂OH
|
C=O
|
HO—H
|
H—OH
|
H—OH
|
CH₂OH

$\xrightarrow{NaBH_4}$

CH₂OH
|
H—C—OH
|
HO—H
|
H—OH
|
H—OH
|
CH₂OH
D-Glucitol

+

CH₂OH
|
HO—C—H
|
HO—H
|
H—OH
|
H—OH
|
CH₂OH
D-Mannitol

A mixture of alditols

$\xrightarrow{\text{3 moles of} \atop PhNHNH_2}$

CH=NNHPh
|
C=NNHPh
|
HO—H
|
H—OH
|
H—OH
|
CH₂OH
D-Fructose phenylosazone
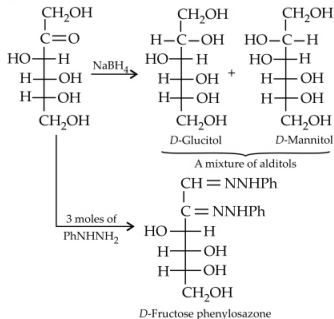
Reducing and Non-reducing Sugars

This is merely a classification based on the reactivity towards oxidising agents like Tollens' reagent, Fehling's solution and Benedict's solution.

Glucose, fructose, maltose, lactose and cellobiose give positive tests by the way of formation of a shiny silver mirror with Tollens' reagent. Blue colour of

the alkaline solution of Benedict's reagent or related Fehling's solution give a red precipitate of Cu_2O. These sugars are called reducing sugars. Sucrose is called non-reducing sugar.

○ Reason for this can be explained as follows :
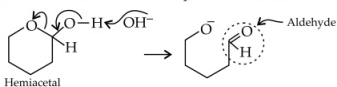
Hemiacetal

This hemiacetal linkage is their in glucose, lactose, cellobiose and maltose.

○ Fructose, on the other hand, also exists as a hemiacetal, which when opens up gives α-hydroxyketone. Such ketones in alkaline medium get rearranged to generate – CHO.
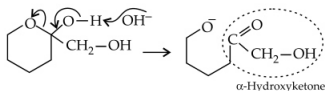
α-Hydroxyketone

Then α-hydroxyketone rearranges to generate aldehyde.

$$\underset{\substack{R \\ \alpha\text{-Hydroxyketone}}}{\overset{\substack{CH_2-OH \\ | \\ C=O \\ |}}{}} \underset{OH^-}{\rightleftharpoons} \underset{\substack{R \\ Enediol}}{\overset{\substack{CH-OH \\ \| \\ C-OH \\ |}}{}} \underset{OH^-}{\rightleftharpoons} \underset{\substack{R \\ Aldehyde}}{\overset{\substack{CH=O \\ | \\ CH-OH \\ |}}{}}$$
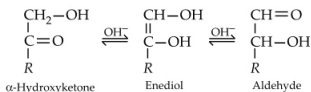
○ Similar rearrangement occurs when dilute solution of glucose is treated with NaOH solution.
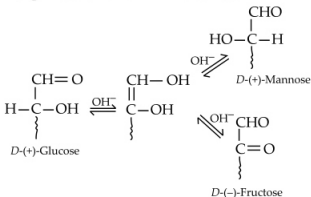
The mixture obtained is almost optically inactive. The same mixture is obtained with D-(+)-glucose or D(+)-mannose or D(–)-fructose.

○ Sucrose on the other hand is a ketal, which does not open in alkaline medium.

OH⁻ → No opening

Reactions of Sucrose

Sucrose
- conc. HCl → $CH_3-CO-CH_2-CH_2-COOH$ Leavulinic acid
- conc. HNO_3 → 6 moles of oxalic acid
- conc. H_2SO_4 → Sugar charcoal
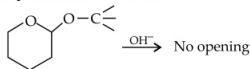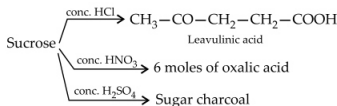
Mutarotation

Two crystalline forms of D-glucose were obtained, one crystallised at room temperature (20-21°C) and had a melting point of 146°C and a specific optical rotation +112°, the other crystallised at temperature above 98°C and had a melting point of 150°C and a specific rotation +19°. When these two crystalline forms were dissolved in water and their optical rotation was measured over time, it was found that optical rotation changes for either of the isomer and becomes a constant at +52.7°. This phenomenon is called **mutarotation**.

Water, being amphoteric in nature helps in this process. The ring opens up and ultimately forms an equilibrium mixture of fixed composition.

Fructose, maltose, lactose, cellobiose also exhibit mutarotation. Sucrose does not show mutarotation.

Hydrolysis of Sucrose and Optical Rotation

When sucrose is hydrolysed, the +ve optical rotation changes to –ve optical rotation. This is because, sucrose hydrolyses to give an equimolar mixture of glucose (+52.7°) and fructose (–92°). In industry, invert sugar means a mixture of glucose and fructose.

Invert sugar is the first choice because

○ it is hygroscopic and therefore, keeps cakes fresh and moist.

○ it resists crystallisation thus, promotes smoothness in candies, icings, etc.

Note : Generally sucrose is called invert sugar.

Invert sugar occurs naturally in honey and fruits. Now-a-days manufacturers produce massive quantities of invert sugar by boiling sucrose solution.

Cellulose

○ It is a polymer of β-D-glucose. Its chair form structure is
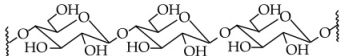
Starch

○ It contains amylose (water soluble component of starch) 20% and amylopectin 80%. Amylose is the polymer of α-D-glucose and has helical structure.

○○

CHEMISTRY MUSING

1. (a) : For a gaseous mixture of ethane and ethene
$$PV = nRT$$
$$\therefore \quad 1 \times 40 = n \times 0.082 \times 400 \Rightarrow n = 1.2195$$
$$\therefore \quad \text{Total number of moles of mixture} = 1.2195$$
Let the moles of ethane and ethene be a, b respectively $\Rightarrow a + b = 1.2195$ ...(i)

$$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
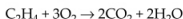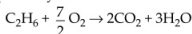
$\therefore$ Moles of O_2 needed for complete reaction of mixture $= \frac{7}{2}a + 3b \Rightarrow \frac{7}{2}a + 3b = \frac{130}{32}$ ...(ii)

By solving eqn. (i) and (ii), we get $a = 0.8085$, $b = 0.4115$
$\therefore$ Mole fraction of ethane $= 0.8085/1.2195 = 0.66$
and mole fraction of ethene $= 1 - 0.66 = 0.34$

2. (c) : $C_2^+(11)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^1)$
Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(7 - 4) = 1.5$
$O_2^{2+}(14)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 = \pi 2p_y^2)$
Bond order $= \frac{1}{2}(10 - 4) = 3$
$Be_2(8)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$
Bond order $= \frac{1}{2}(4 - 4) = 0$
$C_2(12)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2)$
Bond order $= \frac{1}{2}(8 - 4) = 2$
$O_2^{2-}(18)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$(\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^2 = \pi^* 2p_y^2)$
Bond order $= \frac{1}{2}(10 - 8) = 1$
$C_2^-(13)$: $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2), \sigma 2p_z^1$
Bond order $= \frac{1}{2}(9 - 4) = 2.5$
Thus, increasing order of bond strengths is
$$Be_2 < O_2^{2-} < C_2^+ < C_2 < C_2^- < O_2^{2+}$$

3. (d) :
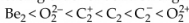
$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \xrightarrow[\text{(Reduction)}]{NaBH_4, CH_3OH} CH_3-\underset{\underset{\displaystyle \text{Propan-2-ol}}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}H}-CH_3$$

$$\xrightarrow[\Delta (-H_2O)]{\text{Conc. } H_2SO_4} CH_3-CH=CH_2$$
$$\text{Prop-1-ene}$$

4. (a) : For an adiabatic change, $TV^{\gamma - 1} = $ constant
$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \qquad \left(\because \gamma = \frac{5}{3} \right)$$
$$T_1 V_1^{2/3} = T_2 V_2^{2/3}$$
or $T_1(1)^{2/3} = T_2(2)^{2/3}$ or $T_2 = \dfrac{T_1}{(2)^{2/3}} = \dfrac{T}{(2)^{2/3}}$

5. (b) : $Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$
$$E_{cell} = 0.2905 \text{ V}$$
Reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[Fe^{2+}]} = \dfrac{0.1}{0.01} = 10$
Using Nernst equation, $E_{cell} = E_{cell}^\circ - \dfrac{0.0591}{n} \log Q$
$$0.2905 = E^\circ - \frac{0.0591}{2} \log 10 \Rightarrow E^\circ = 0.32 \text{ V}$$
$$E^\circ = \frac{0.0591}{n} \log K_{eq} \Rightarrow 0.32 = \frac{0.0591}{2} \log K_{eq}$$
$$K_{eq} = 10^{0.32/0.0295}$$

6. (c) : $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$
$$\underset{(W)}{}$$
$$\underset{(W)}{2NaHSO_3} + Na_2CO_3 \longrightarrow \underset{(X)}{2Na_2SO_3} + H_2O + CO_2$$
$$\underset{(X)}{Na_2SO_3} + S \xrightarrow{\Delta} \underset{(Y)}{Na_2S_2O_3}$$
$$\underset{(Y)}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{(Z)}{Na_2S_4O_6} + 2NaI$$

7. (b) :

$$\underset{\underset{(A)}{(C_5H_{10}O_2)}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2COOH} \xrightarrow{P, Br_2} \underset{(X)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-\overset{\overset{\displaystyle Br}{|}}{C}H-COOH}$$

$$\downarrow -HBr$$

$$\underset{(Z)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} \xleftarrow[O_3, Zn]{-CO_2} \underset{\substack{(Y) \\ \text{(Does not show} \\ \text{geometrical isomerism.)}}}{CH_3-C=CHCOOH}$$

$$\underset{\substack{(CH_3)_2CO \\ \text{(Gives iodoform} \\ \text{test)}}}{} + \underset{\substack{HCHO \\ \text{(Does not give} \\ \text{iodoform test)}}}{}$$
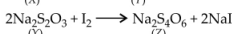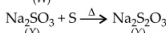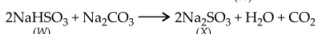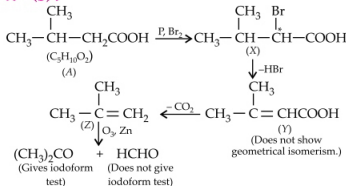
8. (d)

9. (3) : Isotopes have same atomic number but different mass numbers, $^{16}_8O, {}^{18}_8O; {}^{14}_7N, {}^{15}_7N$
Total number of pairs of isotopes = 2
Isobars have same mass number but atomic numbers, $^{40}_{20}Ca, {}^{40}_{21}Sc; {}^{77}_{32}Ge, {}^{77}_{33}As$
Total number of pairs of isobars = 2
Isotones have same number of neutrons.
$^{39}_{19}K, {}^{40}_{20}Ca; {}^{16}_8O, {}^{15}_7N; {}^{77}_{33}As, {}^{78}_{34}Se$
Total number of pairs of isotones = 3
Thus, the value is $\dfrac{(3 \times 2)}{2} = 3$
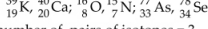
10. (8) : $\underset{\substack{0.1 \text{ mol} \\ 0.1-0.08 = 0.02}}{CH_3NH_2} + \underset{\substack{0.08 \text{ mol} \\ 0}}{HCl} \rightarrow \underset{\substack{0.08 \text{ mol}}}{CH_3\overset{+}{N}H_3Cl^-}$
$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$
$$= -\log(5 \times 10^{-4}) + \log \frac{0.08}{0.02} = 3.903$$
$$pH = 14 - 3.903 = 10.0969$$
$$[H^+] = \text{Antilog} (-10.0969) = 8 \times 10^{-11} \text{ M}$$

CONCEPT BOOSTER

Dear students, I wish you have given your Board Exam very well. Now its time for the tough game. I hope you all will come off with flying colours. I am presenting few conceptual problems in this article. Go through it. Check whether there is any lacuna in your preparation. Correct it. All the very very best!!
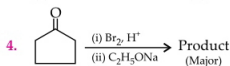
*Arunava Sarkar

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

SINGLE CORRECT ANSWER TYPE

1.

(a) (b)

(c) (d) None of these.

2.

(a) $A = $;

$B = (CH_2)_3 - COOH$

(b) $A = $; $B = $

(c) A & $B = $

(d) A & $B = $
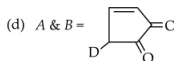
3. Arrange the followings according to the increasing order of reactivity in nucleophilic addition reaction.
   I.   Aldehyde   II.   Acid chloride
   III. Ketone   IV.   Ester
   (a) I < II < III < IV   (b) II < I < III < IV
   (c) IV < III < II < I   (d) None of these.

4.

   Product is

   (a) + CH_3ONa (b)

   (c) (d) + C_2H_5Br

5. Q $\xrightarrow{LAH}$ $\xrightarrow{H_2, Ni}$ P

   (a) $P = $; $Q = $

   (b) P & $Q = $

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

(c) $P =$; $Q =$

(d) None of these.

6. $\xrightarrow[\text{Pt}]{H_2 \text{ (1 equivalent)}}$?

(a)   (b)

(c)   (d)

7. $\xrightarrow[\text{H}_3\text{O}^+]{\substack{H^+ \\ \text{LiAlH}_4}} X$
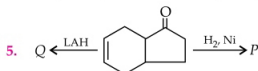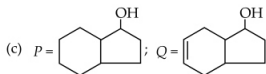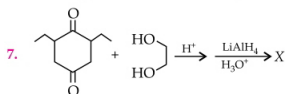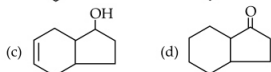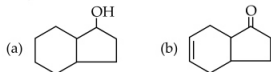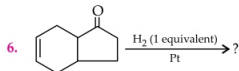
Identify the structure of X.
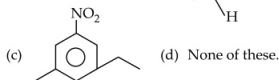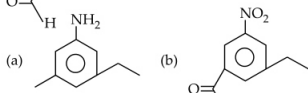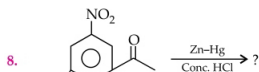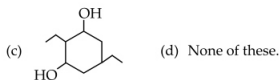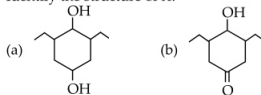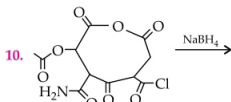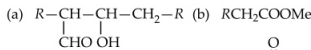
(a)   (b)

(c)   (d) None of these.

8. $\xrightarrow[\text{Conc. HCl}]{\text{Zn–Hg}}$?

(a)   (b)

(c)   (d) None of these.

9. Identify the major product in the following reaction:

$R\text{—CH}_2\text{—CHO}$ + MeCOOEt $\xrightarrow{\text{MeONa}}$? (Major)

(a) $R\text{—CH—CH—CH}_2\text{—}R$ (b) $R\text{CH}_2\text{COOMe}$
$\qquad \quad |\qquad |$
$\qquad \text{CHO OH}$

(c) $R\text{CH}_2\text{COOEt}$ (d)

10. $\xrightarrow{\text{NaBH}_4}$

Identify the product.

(a)   (b)

(c)   (d) None of these.

11. Identify the major product in the following reaction:

 $\xrightarrow{\text{Ph}_3\overset{..}{\text{P}}}$

(a)   (b)

(c)   (d) None of these.

12. + CH$_3$CHO $\xrightarrow{\overline{\text{O}}\text{H}/\text{H}_2\text{O}}$ A

Identify A.

(a)   (b) $\text{CH}_3\text{CH}=$

(c)

(d) None of these.

13. $\xrightarrow[\text{ether}]{\text{LiAlH}_4}$ A

$\xrightarrow[\text{alcohol}]{\text{NaBH}_4}$ B

A and B are respectively

(a) $A =$; $B =$

(b) $A =$; $B =$

(c) $A =$; $B =$

(d) A & $B =$

14. $\xrightarrow{\text{PCC}}$ A

$\xrightarrow{\text{CrO}_3/\text{H}_2\text{SO}_4}$ B

$\xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4}$ C

$\xrightarrow{\text{CrO}_3/\text{Pyridine}}$ D

Identify A, B, C and D.

(a) $A = B =$; $C = D =$

(b) $A = D =$; $B = C =$

(c) $A = D =$; $B = C =$

(d) $A =$; $B =$; $C =$; $D = \text{CO}_2$
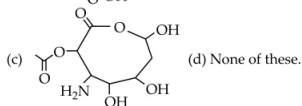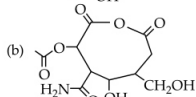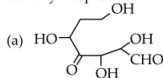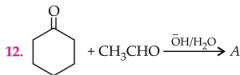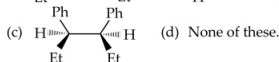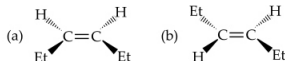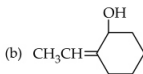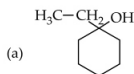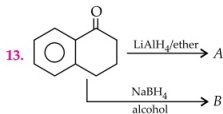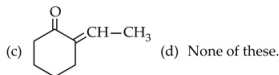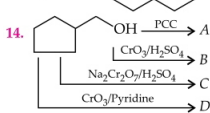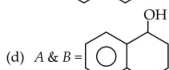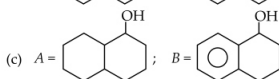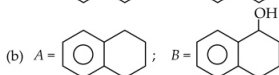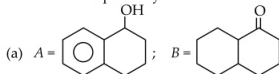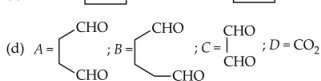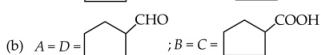
15. Identify S and R in the following sequence of reactions.

 $\xrightarrow{\text{[O]}}$ P $\xrightarrow[\Delta]{\text{NaOH}\atop\text{sodalime,}}$ Q $\xrightarrow[\text{LiAlH}_4]{\text{NaBH}_4}$ S, R

(a) $S = R =$

(b) $S = R =$

(c) $S =$; $R =$

(d) None of these.

16. $\xrightarrow{\text{AlCl}_3}$ $\xrightarrow[180°C]{\text{NH}_2-\text{NH}_2\atop\text{C}_2\text{H}_5\text{ONa}}$
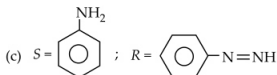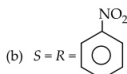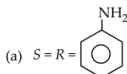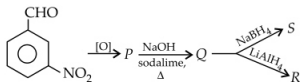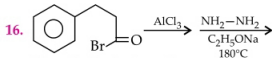
Identify the final product.

(a) (b)

(c) (d) None of these.

17. $\xrightarrow[\text{H}_3\text{O}^+]{\text{LiAlH}_4}$ A

$\xrightarrow[\text{H}_3\text{O}^+]{\text{Sia}_2\text{BH}}$ B
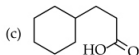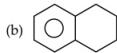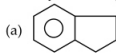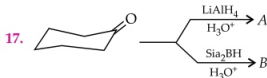
(a) A and B both are *trans* alcohols.
(b) A is *trans* alcohol but B is *cis* alcohol.
(c) A and B both are *cis* alcohols.
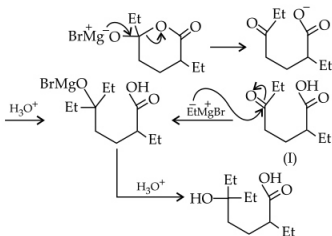(d) A is *cis* alcohol but B is *trans* alcohol.

SOLUTIONS

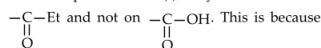**1. (d):**
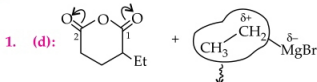
Where will this attack?
At C-1 or at C-2?

For the nucleophilic attack, carbonyl carbon should have large positive charge and also less sterically hindered. Due to the +I effect of –Et group, C-1 is getting less positive charge, so attack will be on C-2.
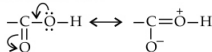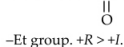
 $+ \text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{THF}}$
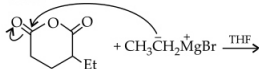
So, answer is (d).

Now the question is at (I), why the attack is on

$-\overset{\underset{\parallel}{O}}{C}-Et$ and not on $-\overset{\underset{\parallel}{O}}{C}-OH$. This is because

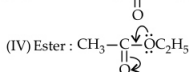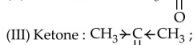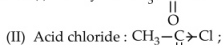the positive charge on the carbonyl carbon is diminished in this way due to the +R effect of oxygen atom of – OH.

Whereas in $-\overset{\underset{\parallel}{O}}{C}-Et$, you have only +I effect of

–Et group. +R > +I.

2. **(b):** MnO_2 is a selective oxidising agent which oxidises allylic or benzylic $-OH$ group into $>C=O$ group whereas Jone's reagent oxidises both 2° and 1° (normal case, allylic or benzylic) $-\overset{\underset{\mid}{\mid}}{C}-OH$ group into $>C=O$ group. Therefore answer is (b).

3. **(d):** (I) Aldehyde : $CH_3 \rightarrow \overset{\underset{\parallel}{O}}{C}-H$;

    (II) Acid chloride : $CH_3 \rightarrow \overset{\underset{\parallel}{O}}{C} \rightarrow Cl$;

    (III) Ketone : $CH_3 \rightarrow \overset{\underset{\parallel}{O}}{C} \leftarrow CH_3$;

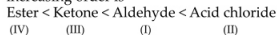   (IV) Ester : $CH_3 - \overset{\underset{\parallel}{O}}{C} \overset{..}{\underset{..}{O}} C_2H_5$

In acid chloride, chlorine atom shows –I effect, thus makes the carbonyl carbon more electron deficient and nucleophilic. In ketone, both the $-CH_3$ groups push electrons to carbonyl carbon and thus decrease the positive charge on the carbonyl carbon.
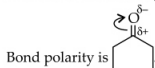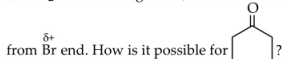In aldehyde, only one $-CH_3$ group pushes electrons to carbonyl carbon and thus decreases

the positive charge on the carbonyl carbon to a smaller extent than that of the ketone. In ketone, carbonyl carbon is more sterically hindered than that of the aldehyde.
In ester, positive charge on carbonyl carbon is maximum diminished due to the +R effect of $-\overset{..}{O}C_2H_5$ group. So, this is least reactive for the nucleophilic addition reaction. So, overall increasing order is

Ester < Ketone < Aldehyde < Acid chloride
(IV)   (III)   (I)   (II)

4. **(c) :** Br_2 is $\overset{\delta+}{Br}-\overset{\delta-}{Br}$. In general, attack will take place

from $\overset{\delta+}{Br}$ end. How is it possible for ?

Bond polarity is .

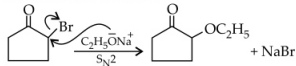Br_2 addition will not take place across $>C=O$. But across carbon-carbon multiple bond, Br_2 addition can take place. So, there must be something by which we can produce carbon-carbon multiple bond in the ring. But what is that? Take the enol content of cyclopentanone.
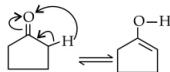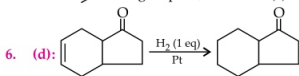

Now,
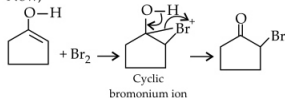
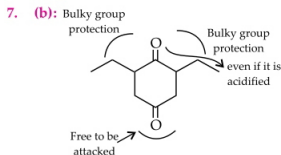To generate the $>C=O$ bond again, Br^+ opens the bond in that manner.

5. **(c) :** $LiAlH_4$ reduces $>C=O$ to $-CHOH$ but cannot reduce double bond (=). On the other hand, Ni/H_2 can reduce both the double bond as well as $>C=O$ group. So, answer is (c).
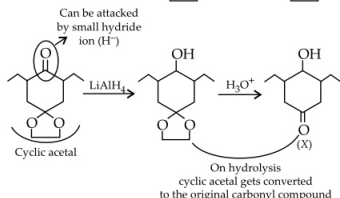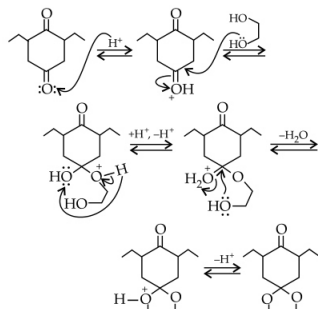
6. **(d):**

In the presence of Pt when H_2 is blown, it can only do the syn-addition reaction as here through the

'occlusion', H_2 is adsorbed in Pt which comes out from the surface to cause the reduction (this is not the case with Ni/H_2). Two hydride transfer is required to reduce $>C=O$ which is not possible with 1 eq. of H_2.

7. (b):

Bulky group protection

Bulky group protection even if it is acidified

Free to be attacked

HO—CH$_2$—CH$_2$—OH cannot attack there due to steric factor.

Can be attacked by small hydride ion (H⁻)

Cyclic acetal

$\xrightarrow{\text{LiAlH}_4}$

$\xrightarrow{\text{H}_3\text{O}^+}$ (X)

On hydrolysis cyclic acetal gets converted to the original carbonyl compound

8. (a): Zn-Hg/HCl can reduce aldehyde, ketone as well as –NO_2 group. Hence (a) is the correct answer.

9. (a): In the presence of a strong base (MeO⁻), aldehydes containing α-H would prefer to undergo enolate formation rather than going into the reaction with ester.
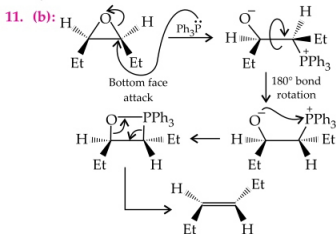

β-Hydroxyaldehyde
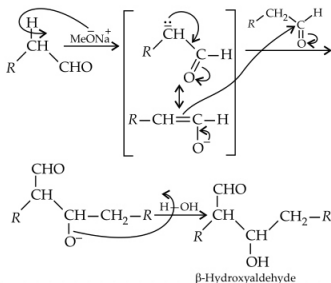
Additional Knowledge : The reaction between the aldehyde and the ester can be made possible through Stork enamine reaction.
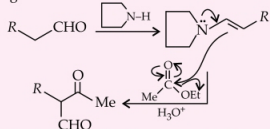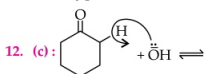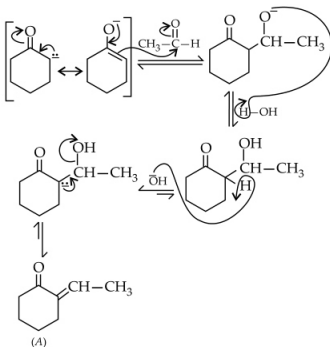

(EtO⁻ is not so good leaving group but the reaction still managed to accomplish.)

10. (b): NaBH$_4$ reduces acid chloride and $>C=O$ groups. Anhydride, acid amide cannot be reduced by NaBH$_4$. So, answer is (b).

11. (b):

Bottom face attack

180° bond rotation

The driving force for the bond rotation is mainly the multiple bond formation between phosphorus and oxygen.

12. (c):

(A)

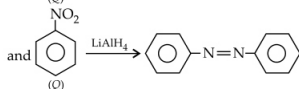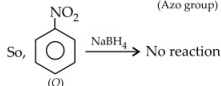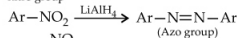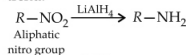**13. (d):** LiAlH$_4$ and NaBH$_4$ both can reduce $>$C$=$O to $>$CH$-$OH but cannot affect $>$C$=$C$<$.
So, correct answer is (d).

14. (b): Na$_2$Cr$_2$O$_7$/H$_2$SO$_4$ and CrO$_3$/H$_2$SO$_4$ are strong oxidising agents and convert 1° alcohol to carboxylic acid. Presence of pyridine lessen the activity of an oxidising agent. So, here 1° alcohol is converted to aldehyde. So, correct option is (b).

15. (d):
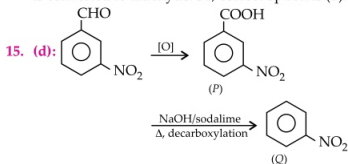
Now, NaBH$_4$ does not reduce aliphatic or aromatic nitro group. With LiAlH$_4$ it follows the following trend.

$$R-NO_2 \xrightarrow{\text{LiAlH}_4} R-NH_2$$
Aliphatic nitro group

$$Ar-NO_2 \xrightarrow{\text{LiAlH}_4} Ar-N=N-Ar$$
(Azo group)

So,

16. (a):
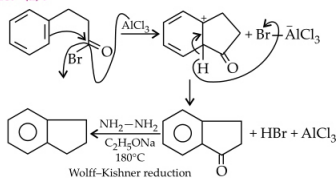
So, correct option is (a). This compound is known as indane.

17. (b): There are three major attributes:
(i) LiAlH$_4$ is an unhindered reducing agent.
(ii) Sia$_2$BH is a hindered reducing agent.
(iii)

Can cause 1,3-diaxial interaction for bulky reducing agent.

LiAlH$_4$ attacks from the axial side to give thermodynamically more stable equatorial *i.e. trans* alcohol.

trans alcohol
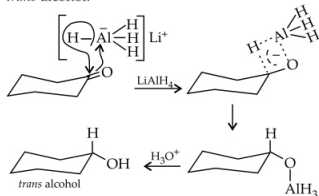
Due to 1,3-diaxial interaction, Sia$_2$BH attacks from the less hindered equatorial side.
Eventually, we get less stable axial alcohol *i.e. cis* alcohol.
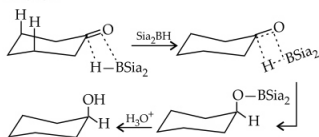
Sia$_2$BH is disecondary isoamyl boron hydride (amyl = 5)

$$\left(CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}- \right)_2 BH$$

■■

Y?U ASKED
WE ANSWERED

Do you have a question that you just can't get answered?
Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.
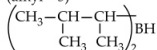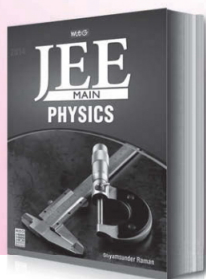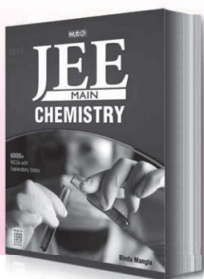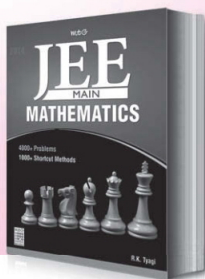The best questions and their solutions will be printed in this column each month.

Q1. Is there any relationship between standard reduction potential and metallic character of an element(metal)?
*– Biswajit Mandal*

Ans. There does not exist any mathematical relationship between standard reduction potential ($E°$) of an element and its metallic character but we can predict the metallic nature from the value of standard reduction potential. Metallic character is the tendency of an element to lose electron whereas $E°$ gives the tendency to get reduced (*i.e.*; gain electrons). So, higher the $E°$ value, lesser is the metallic character or vice-versa.

Q2. Why do the silver items get tanned when exposed to air? How do the instant silver shine liquids work on these silver items?
– Arunav Sahay, Mumbai

Ans. When silver is exposed to air, it combines with sulphur or sulphur containing compounds in the air and form silver sulphide.

$$2Ag + S \longrightarrow \underset{\text{black}}{Ag_2S}$$
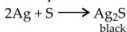
Instant 'silver shine liquids' or commercial 'silver dips' are available in market which remove stains without rubbing the silver. The active ingredient of these 'silver dips' is thiourea, a sulphur-scavenger which draws the sulphur out of tarnished silver. *i.e.*; reverses the tarnishing process *e.g.*; Tarn *X* contains thiourea, a detergent and sulfamic acid. Goddard's Long shine silver polish in liquid form contains 2% ammonia, 2-butoxyethanol and less than 0.3% DMDM hydantoin.

2-Butoxyethanol

DMDM hydantoin
IUPAC name
1,3-Bis(hydroxymethyl)-5,
5-dimethylimidazolidine-2, 4-dione
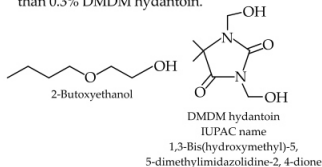
Q3. Is the colour changing phenomenon of chameleon is a chemical reaction? If yes, then describe it.
– Diganta Bhaskar, Kolkata

Ans. It is a physical change. Pre-existing pigments are moved to and from the surface of the skin, but the pigments themselves do not change.
Chameleons can change their skin colour with the help of specialized cells, chromatophores, which contain pigments in their cytoplasm, in three layers below their transparent outer skin :
– The chromatophores in the upper layer, called xanthophores and erythrophores, contain yellow and red pigments, respectively.
– Below the chromatophores is a second layer of chromatophores called iridophores or guanophores; these contain guanine, appearing blue or white.
– The deepest layer of chromatophores, called melanophores, contain the dark pigment melanin, which controls how much light is reflected.
A change in skin colouration is usually induced by factors like light, temperature, mood and health of the chameleon.

Q4. Which chemical is used in 'Dry Cleaning' industries?
– Vishwa Pratap, Lucknow

Ans. Dry cleaning is any cleaning process for clothing and textiles using a chemical solvent other than water. The solvent used is typically tetrachloroethylene (perchloroethylene), which the industry calls "perc".

Perchloroethylene
(perc)

The dry cleaning industry had adopted "perc" for short, as the ideal solvent. It has excellent cleaning power and is stable, non-flammable, and gentle to most garments. Perc, however, was incidentally the first chemical to be classified as a carcinogen. Thus, the dry cleaning industry is in the process of replacing perc with other chemicals and/or methods.
Glycol ethers *e.g.*; dipropylene glycol tertiary-butyl ether (DPTB) are in many cases more effective than 'perc' and in all cases more environmentally friendly.

DPTB
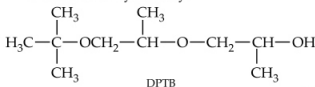
PRACTICE PAPER 2Q14

BITSAT

1. The weight of 1g-equivalent of V_2O_5 used in the reaction:
$$Zn + V_2O_5 \longrightarrow ZnO + V \text{ is (At. wt. of } V = A)$$

(a) $\dfrac{A}{5}$

(b) $\dfrac{A+80}{5}$

(c) $\dfrac{2A+80}{5}$

(d) $\dfrac{2A+80}{10}$

2. ⬡—CH_2OH on dehydration with conc. H_2SO_4 predominantly forms

(a) ⬡=CH_2

(b) ⬡—CH_3

(c) ⬡—CH_3

(d) ⬡—CH_3

3. A section of the periodic table is given below with elements A, B and X, Y in two groups. Which of the bonds given below is the least polar?
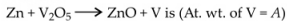
Group I	Group II
A	X
B	Y

(a) AX

(b) AY

(c) BX

(d) BY

4. Which of the following compounds have two lone pairs of electrons?
$$\underset{I}{NO_2^-}, \underset{II}{OF_2}, \underset{III}{XeF_2}, \underset{IV}{ICl_3}$$
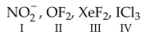
(a) I and III

(b) II and III

(c) II and IV

(d) I and IV

5. The correct statement about the compounds A, B and C is

```
     COOCH3              COOH
H ——|—— OH        H ——|—— OH
H ——|—— OH        H ——|—— OH
     COOH              COOCH3
      (A)               (B)
```

```
       COOH
  H ——|—— OH
  HO ——|—— H
       COOCH3
        (C)
```
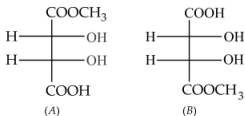
(a) A and B are identical.

(b) A and B are diastereomers.

(c) A and C are enantiomers.

(d) A and B are enantiomers.

6. The rate of change of concentration of (A) for reaction: $A \longrightarrow B$ is given by
$$\frac{-d[A]}{dt} = k[A]^{1/3}$$

The half-life period of the reaction will be

(a) $\dfrac{3[A_0]^{2/3}[(2)^{2/3}-1]^2}{(2)^{5/3}k}$

(b) $\dfrac{\frac{3}{2}[A_0]^{2/3}[(2)^{2/3}-1]}{k}$

(c) $\dfrac{3[A_0]^{2/3}[(2)^{2/3}-1]}{(2)^{5/3}k}$

(d) $\dfrac{\frac{2}{3}[A_0]^{3/2}[(2)^{2/3}-1]}{k}$

7. The decreasing order of reactivity of the following compounds towards OH^- ions is
m-Nitrobromobenzene(I);
2, 4, 6-Trinitrobromobenzene(II);
p-Nitrobromobenzene(III); and
2, 4-Dinitrobromobenzene (IV);

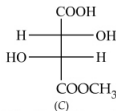(a) I > II > III > IV

(b) II > IV > III > I

(c) IV > II > III > I

(d) II > IV > I > III

8. M_2O_x, a gaseous oxide, consists of 36.32% oxygen. In an experiment, the ratio of the rates of diffusion of carbon dioxide and that of oxide M_2O_x is found to be 4.7 : 4.6. The exact atomic weight of the element M is

(a) 14

(b) 17

(c) 28

(d) 31

9. Given: $\Delta G° = -nFE°_{cell}$ and $\Delta G° = -RT \ln K$
The value of $n = 2$ will be given by the slope of which line in the given figure?
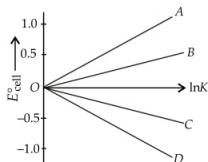
(a) *OA* (b) *OB* (c) *OC* (d) *OD*

10. Which of the following pairs of molecules have practically the same mass?
(a) D_2O and HTO (b) H_2O and HTO
(c) H_2O and D_2O (d) DTO and HDO

11. The final product (Y) formed in the reaction:

(a)   (b)

(c)   (d)

12. Which of the following forms complex which is square planar and diamagnetic in nature?
(a) Cr^{2+} in weak field ligand
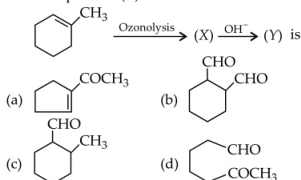(b) Ag^{2+} in weak or strong field ligand
(c) Ni^{2+} in strong field ligand
(d) Co^{2+} in strong field ligand

13. In a measurement of quantum efficiency of photosynthesis in green plants, it was found that 8 quanta of red light at 6850 Å were needed to evolve 1 molecule of O_2. The average energy storage in the photosynthesis process is 112 kcal/mol O_2 evolved. Hence, the energy conversion efficiency in this experiment is
(a) 20% (b) 25% (c) 33.5% (d) 100%

14. An ideal gas with pressure P, volume V, and temperature T is expanded isothermally to a volume $2V$ and a final pressure is P_I. If the same gas is expanded adiabatically to a volume $2V$, and the final pressure is P_{II} and the ratio of specific heats for the gas is 1.67, then the ratio of P_{II}/P_I is

(a) $\dfrac{1}{(2)^{0.67}}$ (b) $(2)^{0.67}$

(c) $\left(-\dfrac{1}{2}\right)^{-0.67}$ (d) $\dfrac{1}{2^{-0.67}}$

15. An amide, C_3H_7NO upon acid hydrolysis gives an acid, $C_3H_6O_2$ which on reaction with Br_2/P gives α-bromo acid which when boiled with aq. OH^- followed by acidification gives lactic acid. What is the structural formula of amide?

(a)

(b)

(c)

(d)
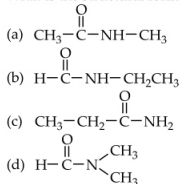
16. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other in
(a) Ti^+, Ti^{3+} (b) Cu^+, Cu^{2+}
(c) Cr^{2+}, Cr^{3+} (d) V^{2+}, VO^{2+}

17. Choose the correct comparison of heat of hydrogenation for the following alkenes:
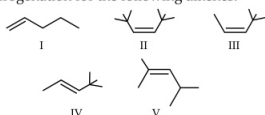
(a) II < IV < III < V < I (b) III < IV < I < V < II
(c) V < IV < III < I < II (d) IV < V < I < III < II

18. Three elements A, B and O crystallise in *ccp* lattice with atoms A at corners, atoms B at body centre and atoms O at the edge centre. Chemical formula of solid is
(a) AB_2O_4 (b) ABO_4 (c) A_2BO_3 (d) ABO_3

19. For the reaction: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H = -93.6$ kJ mol^{-1}, the concentration of H_2 at equilibrium can be increased by
(i) lowering the temperature
(ii) increasing the volume of the system
(iii) adding N_2 at constant volume
(iv) adding H_2 at constant volume
(a) (i) and (iv) are correct.
(b) (ii) only is correct.
(c) (i), (ii) and (iii) are correct.
(d) (iii) and (iv) are correct.

20. An optically active amine (A) of molecular formula $C_4H_{11}N$ is subjected to Hofmann's exhaustive methylation process and following hydrolysis an alkene (B) is produced which upon ozonolysis

and subsequent hydrolysis yields formaldehyde and propanal. The amine (A) is

(a) $CH_3-CH-CH_2CH_3$
        |
       NH_2

(b) $CH_3-NH-CH-CH_3$
              |
             C_2H_5

(c) $CH_3-N-CH_2CH_3$
           |
          C_3H_7

(d) $CH_3CH_2CH_2CH_2-NH_2$
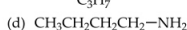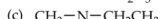
21. An example of a condensation homopolymer is
   (a) bakelite
   (b) melamine-formaldehyde resin
   (c) alkyd resin
   (d) perlon or nylon-6

22. Which of the following statements is correct?
   (a) SF_6 does not react with water.
   (b) OF_6 is d^2sp^3-hybridized.
   (c) $S_2O_3^{2-}$ is a linear ion.
   (d) There is no π-bonding in SO_4^{2-}.

23. Two beakers (A) and (B) containing pure water and aqueous solution of sugar respectively are placed in a closed glass container. The temperature of the container is kept constant. It is observed that
   (a) level of water in beaker (A) decreases and that in beaker (B) increases with time.
   (b) level of water in beakers (A) and (B) remains constant with time.
   (c) level of water in beaker (A) increases and that in beaker (B) decreases with time.
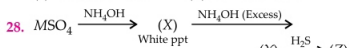   (d) level of water in both the beakers decreases with time.

24. Which of the following structures for a nucleotide is not correct?
   (a) Cytosine-Ribose-Phosphate
   (b) Uracil-2-Deoxyribose-Phosphate
   (c) Uracil-Ribose-Phosphate
   (d) Thymine-2-Deoxyribose-Phosphate

25. Which of the following is not metabolized in the body?
   (a) Sucrose   (b) D-Glucose
   (c) L-Glucose   (d) Aspartame

26. Which of the following compounds possesses the C—H bond with the lowest bond dissociation energy?
   (a) Toluene   (b) Benzene
   (c) n-Pentane   (d) 2,2-Dimethylpropane

27. The coagulation value in millimoles per litre of electrolytes used for the coagulation of As_2O_3 are as given:

I. $NaCl = 52$ II. $KCl = 5$
III. $BaCl_2 = 0.69$ IV. $MgSO_4 = 0.22$
The correct order of their flocculating power is
   (a) I > II > III > IV   (b) I > II > III = IV
   (c) IV > III > II > I   (d) IV = III > II > I

28. $MSO_4 \xrightarrow{NH_4OH} (X) \xrightarrow{NH_4OH \ (Excess)} (Y) \xrightarrow{H_2S} (Z)$
   White ppt

(M) and (Z) are respectively,
   (a) Ca, ZnS   (b) Zn, ZnS
   (c) Al, Al_2S_3 (d) Fe, FeS

29. 0.10 g of an organic compound containing phosphorus gave 0.222 g of $Mg_2P_2O_7$. The percentage of phosphorus in it is
   (a) 7.5   (b) 15   (c) 31   (d) 62

30. In the titration of sodium carbonate with hydrochloric acid taken in burette, the indicator used is/are
   (a) phenolphthalein for first equivalence point and methyl orange for second equivalence point.
   (b) methyl orange for first equivalence point and phenolphthalein for second equivalence point.
   (c) either methyl orange or phenolphthalein for both equivalence points.
   (d) thymol blue for both equivalence points.

31. The compound, $C_3H_6O_2$ is mixed with a dilute solution of 2% NaOH containing a drop of phenolphthalein and boiled. The pink colour is discharged. The compound could be
   (a) CH_3COCH_3 (b) $HCOOC_2H_5$
   (c) C_2H_5COOH (d) Either (a) or (b)

32. Certain volume of a gas exerts some pressure on walls of a container at constant temperature. It has been found that by reducing the volume of the gas to half of its original value, the pressure becomes twice that of initial value at constant temperature. This is because
   (a) the weight of the gas increases with pressure
   (b) velocity of gas molecules decreases
   (c) more number of gas molecules strike the surface per second
   (d) gas molecules attract one another.

33. Which of the following will form a cell with the highest voltage?
Given: $E^{\circ}_{Co^{2+}/Co} = -0.28$ V, $E^{\circ}_{Ag^+/Ag} = 0.80$ V
   (a) 1 M Ag^+, 1 M Co^{2+}
   (b) 2 M Ag^+, 2 M Co^{2+}
   (c) 0.1 M Ag^+, 2 M Co^{2+}
   (d) 2 M Ag^+, 0.1 M Co^{2+}

34. Two liquids A and B have vapour pressure in the ratio $p_A^\circ : p_B^\circ = 1 : 2$ at a certain temperature. Suppose that we have an ideal solution of A and B in the mole fraction ratio $A : B = 1 : 2$, the mole fraction of A in the vapour in equilibrium with the solution at the given temperature is
(a) 0.25 (b) 0.2 (c) 0.5 (d) 0.33

35. Identify (B) in the following sequence of reactions:

(a)

(b)

(c)

(d)
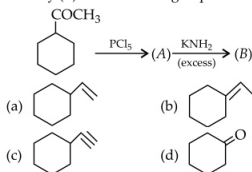
36. n-Butane is produced by monobromination of ethane followed by the Wurtz reaction. The volume of ethane at NTP required to produce 55 g n-butane; if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield will be
(a) 44.9 L (b) 50.5 L (c) 55.5 L (d) 39.6 L

37. The pair of compounds which cannot exist together in solution is
(a) $NaHCO_3$ and $NaOH$
(b) $NaHCO_3$ and H_2O
(c) $NaHCO_3$ and Na_2CO_3
(d) Na_2CO_3 and $NaOH$

38. The electronegativity of the following elements increases in the order
(a) C, N, Si, P   (b) N, Si, C, P
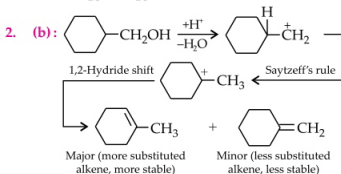(c) Si, P, C, N   (d) P, Si, N, C

39. During the formation of the N_2O_4 dimer from two molecules of NO_2, the odd electrons, one in each of the nitrogen atoms of the NO_2 molecules, get paired to form a
(a) weak N–N bond, two N–O bonds become equivalent and the other two N–O bonds become non-equivalent.
(b) weak N–N bond and all the four N–O bonds become equivalent.
(c) weak N–N bond and all the four N–O bonds become non-equivalent.
(d) strong N–N bond and all the four N–O bonds become non-equivalent.

40. The aqueous solution of which of the following salts will have the lowest pH?
(a) $NaClO$ (b) $NaClO_2$
(c) $NaClO_3$ (d) $NaClO_4$

SOLUTIONS

1. **(d)** : $10e^- + (V^{+5})_2 \longrightarrow 2V^0$
$\therefore\ E = \dfrac{M}{10} = \dfrac{2A + 80}{10}$

2. **(b)** :

Major (more substituted alkene, more stable) + Minor (less substituted alkene, less stable)

3. **(b)** : Electronegativity decreases down the group, and it increases across a period and remains almost same along a diagonal. Therefore atoms A and Y have little difference in their electronegativities and hence AY bond is least polar.

4. **(c)**

5. **(d)** : Rotation of (B) through 180° within the plane of the paper gives (D) which is an enantiomer of (A).
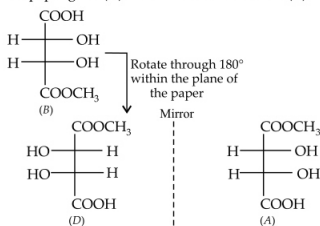
Thus (A) and (B) are enantiomers.

6. **(c)** : $\dfrac{-d[A]}{dt} = k[A]^{1/3} \Rightarrow -\int \dfrac{d[A]}{[A]^{1/3}} = \int k\, dt$

$\Rightarrow\ -\dfrac{3}{2}[A]^{2/3} = kt + C$ ...(i)

At $t = 0$; $[A] = [A_0]$

Then, $-\dfrac{3}{2}[A_0]^{2/3} = C$

Putting the value of C in eq. (i), we get

$-\dfrac{3}{2}[A]^{2/3} = kt - \dfrac{3}{2}[A_0]^{2/3}$

$\Rightarrow\ kt = \dfrac{3}{2}[A_0]^{2/3} - \dfrac{3}{2}[A]^{2/3}$

At $t = t_{1/2}$; $[A] = \dfrac{[A_0]}{2}$

$\therefore\ kt_{1/2} = \dfrac{3}{2}[A_0]^{2/3} - \dfrac{3}{2}\left[\dfrac{A_0}{2}\right]^{2/3}$

$$\Rightarrow \quad kt_{1/2} = \frac{3}{2}\left[[A_0]^{2/3} - \frac{[A_0]^{2/3}}{(2)^{2/3}}\right]$$

$$\Rightarrow \quad t_{1/2} = \frac{3}{2k}[A_0]^{2/3}\left(1 - \frac{1}{(2)^{2/3}}\right)$$

$$\Rightarrow \quad t_{1/2} = \frac{3[A_0]^{2/3}}{2k}\left[\frac{2^{2/3} - 1}{2^{2/3}}\right]$$

$$\therefore \quad t_{1/2} = \frac{3[A_0]^{2/3}}{k}\left[\frac{2^{2/3} - 1}{2^{5/3}}\right]$$

7. (b) : Reactivity decreases as the number of –NO$_2$ groups at *o*- and *p*-positions with respect to –Br decreases. *m*-Nitrobromobenzene is, however, less reactive than the *p*-nitrobromobenzene since the –NO$_2$ group at *m*-position cannot stabilize the intermediate carbanion by resonance. Thus, the order is II > IV > III > I.

8. (a) : Equivalent weight of the element
$$= \frac{63.68}{36.32} \times 8 = 14.03 \qquad (\text{\textit{Oxide formation method}})$$
Molecular weight of oxide can be calculated with the help of Graham's law of diffusion :

$$\frac{r_{CO_2}}{r_{M_2O_x}} = \sqrt{\frac{\text{Mol. wt. of } M_2O_x}{\text{Mol. wt. of } CO_2}}$$

or $\quad \dfrac{4.7}{4.6} = \sqrt{\dfrac{\text{Mol. wt. of } M_2O_x}{44}}$

$\Rightarrow$ Mol. wt. of $M_2O_x = 45.93$
Atomic weight of the element, $M = E \times x$
Therefore, $2(E \times x) + 16x = 45.93$
$$x(2E + 16) = 45.93$$
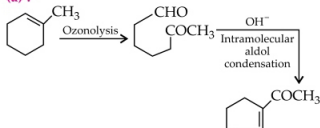$$x = \frac{45.93}{2 \times 14.03 + 16} \approx 1$$

Atomic weight of the element,
$M = E \times x = E \times 1 = 14$

9. (b) : $-nFE^\circ_{cell} = -RT \ln K$ or $E^\circ_{cell} = \dfrac{RT}{nF} \ln K$

Plot of E°_{cell} *vs* ln K will have slope $\dfrac{1}{2}\dfrac{RT}{F}$.

10. (a) : D$_2$O or (^{2}H)$_2$O and HTO or (^{1}H^{3}H)O have practically the same mass.

11. (a) :

12. (c) : Cr^{2+} in weak field ligand has 4 unpaired electrons.
Ag^{2+} in weak or strong field ligand has 1 unpaired electron.
Ni^{2+} in strong field ligand has no unpaired electrons.
Co^{2+} in strong field ligand has 1 unpaired electron.
Hence, Ni^{2+} in strong field ligand, forms complex which is square planar and diamagnetic in nature.

13. (c) : $E = \dfrac{hc}{\lambda} = \dfrac{(6.63 \times 10^{-34})(3 \times 10^8)}{(6850 \times 10^{-10})} = 2.90 \times 10^{-19}$ J

Energy of eight quanta $= 8 \times 2.90 \times 10^{-19}$ J
$= 2.32 \times 10^{-18}$ J

Energy storage (J/molecule) $= \dfrac{112 \times 4.184 \times 10^3}{6.023 \times 10^{23}}$
$= 7.78 \times 10^{-19}$ J/molecule

Energy conversion efficiency
$= \dfrac{\text{Energy evolved}}{\text{Total energy}} \times 100 = \dfrac{7.78 \times 10^{-19}}{2.32 \times 10^{-18}} \times 100 = 33.5\%$

14. (a) : For an isothermal process
$PV = $ constant
$P_1V_1 = P_2V_2$
$PV = P_1 \times 2V$ or $\dfrac{P}{P_1} = 2$ $\qquad \ldots(i)$

For an adiabatic process
$PV^\gamma = $ constant $\qquad (\gamma = 1.67)$
$PV^\gamma = P_{II}(2V)^\gamma$ or $\dfrac{P}{P_{II}} = 2^\gamma$ $\qquad \ldots(ii)$

Dividing (i) by (ii)

$\dfrac{P_{II}}{P_I} = \dfrac{2}{2^\gamma}$ or $\dfrac{P_{II}}{P_I} = \dfrac{1}{2^{\gamma-1}} = \dfrac{1}{(2)^{0.67}}$

15. (c) :
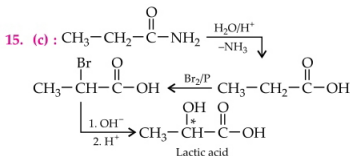
16. (d) : Ti$^+$ does not exist, Cu^{2+} is more stable than Cu$^+$ as evident from their electrode potential. Cr^{3+} is again more stable than Cr^{2+} in aqueous solution. Oxidation state of V in VO^{2+} is + 4. V^{2+} is more stable than V^{4+} in aqueous solution.

17. (c) : Greater is the stability of alkene, lower the heat of hydrogenation.

Out of *cis* and *trans* isomers, *trans* isomer is more stable than *cis* isomer in which two alkyl groups lie on the same side of the double bond and hence cause steric hindrance, therefore, heat of hydrogenation of *trans* isomer is *less* than that of *cis* isomer.
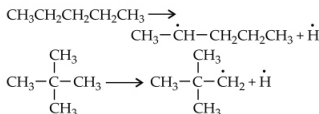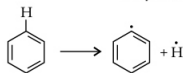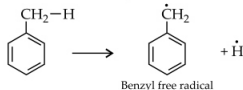

V	IV	III	I
7-hyperconjugative Hs	3-hyperconjugative Hs	2-hyperconjugative Hs	

II
No hyperconjugative Hs
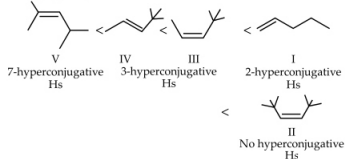
18. (d) : Number of atoms $A = \dfrac{1}{8} \times 8 = 1$

Number of atoms B at body centre = 1

Number of atoms O at edge centre

$= \dfrac{1}{4} \times 12 = 3$

$\therefore$ Formula of compound = ABO_3

19. (a) : For the reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3;$ $\quad \Delta H = -93.6 \text{ kJ mol}^{-1}$

The reaction is exothermic in nature. According to Le Chatelier's principle, lowering of pressure favours the backward reaction or increase in volume favours the backward reaction (when $n_p < n_r$).

Also addition of H_2 at constant volume increases the concentration of H_2 at equilibrium.

20. (a) : The only optically active molecule is

$CH_3-CH_2-CH-CH_3$

$\qquad\qquad\qquad |$

Hofmann's $\qquad NH_2$

exhaustive $\qquad (A)$

methylation $\downarrow$

$CH_3-CH_2-CH-CH_3$ $\quad\xrightarrow{AgOH, \Delta}$

$\qquad\qquad |$

$\qquad\quad N^+$

$\quad H_3C \quad CH_3$

$\qquad\quad CH_3$

$CH_2=CH-CH_2-CH_3$
$\qquad\qquad\qquad (B)$

$\downarrow O_3$

$\downarrow$ Zn/H$_2$O
$\quad$ –ZnO

HCHO + CH$_3$CH$_2$CHO
Formaldehyde $\quad$ Propanal

21. (d) : Nylon-6 is a condensation homopolymer since it is obtained by condensation polymerization of only one type of monomer, *i.e.*, caprolactum.

22. (a) : SF_6 is thermally stable and chemically inert due to the reason that the six F atoms protect the sulphur atom from attack by the reagents.

23. (a) : Boiling point of a solution is always greater than that of pure solvent thus the rate of evaporation in beaker (*A*) (pure solvent) will be more than in beaker (*B*) (solution). But the rate of condensation remains the same for both the beakers. Therefore the level of water in beaker (*A*) decreases and that in beaker (*B*) increases with time.

24. (b) : Uracil is present only in RNA which contains ribose as the sugar. Thus, nucleotide given in option (b) is incorrect.

25. (c) : *L*-Sugars are not metabolized in the body.

26. (a) : C−H bond dissociation energy is the lowest where free radical produced is the most stable.

Benzyl free radical

$CH_3CH_2CH_2CH_2CH_3 \longrightarrow$
$\qquad\qquad CH_3-\overset{\bullet}{C}H-CH_2CH_2CH_3 + \overset{\bullet}{H}$

$\qquad CH_3 \qquad\qquad\qquad CH_3$
$\qquad\quad | \qquad\qquad\qquad\qquad |$
$CH_3-C-CH_3 \longrightarrow CH_3-\overset{\bullet}{C}-CH_2 + \overset{\bullet}{H}$
$\qquad\quad | \qquad\qquad\qquad\qquad |$
$\qquad CH_3 \qquad\qquad\qquad CH_3$

Out of all these free radicals, benzyl free radical is the most stable since it is stabilized by resonance. Thus, toluene has the lowest C−H bond dissociation energy.
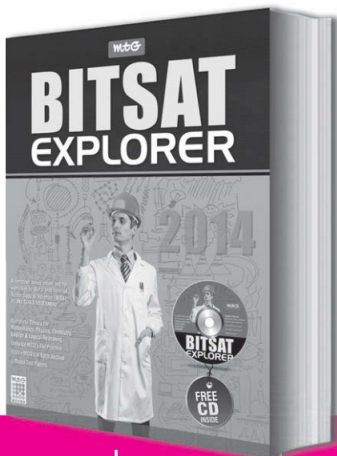
27. (c) : Smaller is the coagulation value of an electrolyte, greater is its coagulating or precipitating power. Therefore, the correct order is IV > III > II > I.

28. (b) :

$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow{NH_4OH \text{ (excess)}}$
$\qquad\qquad\qquad\qquad\quad$ White ppt
$\qquad\qquad\qquad\qquad\quad (X)$

$ZnS + 2NH_4OH \xleftarrow{H_2S} (NH_4)_2ZnO_2 \longleftarrow$
$\quad (Z) \qquad\qquad\qquad\qquad (Y)$

29. (d) : Percentage of phosphorus

$$= \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{Mass of organic compound}} \times 100$$

$$= \frac{62}{222} \times \frac{0.222}{0.10} \times 100$$

$$= 62\%$$

30. (a) : In the titration of sodium carbonate with hydrochloric acid, first equivalence point appears at pH of about 8.3, hence phenolphthalein is used as indicator for first equivalence point. Whereas second equivalence point appears at pH of about 3.9, hence methyl orange is used as indicator for second equivalence point.
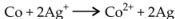
31. (b) :

$$HCOOC_2H_5 + H_2O \xrightarrow{OH^-} HCOOH + C_2H_5OH$$

Acid reacts with NaOH.

Pink

+ HCOO⁻

Colourless
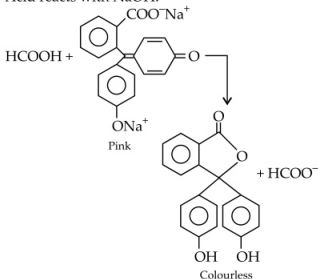
32. (c) : As the volume is decreased, pressure increases because more number of molecules strike the surface per second.

33. (d) : $E°_{Co^{2+}/Co} = -0.28\ V$, $E°_{Ag^+/Ag} = 0.80\ V$

Hence cobalt is anode. *i.e.* oxidation takes place on cobalt electrode *i.e.* cell reaction is

$$Co + 2Ag^+ \longrightarrow Co^{2+} + 2Ag$$

$$\therefore\quad E_{cell} = E°_{cell} - \frac{RT}{nF} \ln \frac{[Co^{2+}]}{[Ag^+]^2}$$

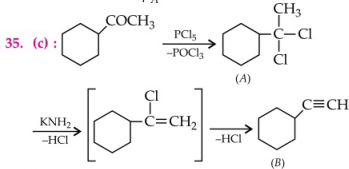Less is the factor $[Co^{2+}]/[Ag^+]^2$, greater is the E_{cell}.

34. (b) : Since the ratio of $p°_A$ and $p°_B$ is 1 : 2 and mole fraction is 1 : 2 therefore,

partial pressure of A ($p_A{}'$) = $p°_A x_A$ and

partial pressure of B ($p_B{}'$) = $p°_B x_B$ are related as

$$p_B{}' = 4p_A{}'$$

$$P = p_A{}' + p_B{}' = p_A{}' + 4p_A{}' = 5p_A{}'$$

The mole fraction of A in the vapour in equilibrium with solution (according to Dalton's law of partial pressure) is

$$x_A{}' = \frac{p_A{}'}{P} = \frac{p_A{}'}{5p_A{}'} = \frac{1}{5} = 0.2$$

35. (c) :

36. (c) : $C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$
    30 g   109 g

$2C_2H_5Br + 2Na \longrightarrow C_4H_{10} + 2NaBr$
  2 × 109 g   58 g

55 g butane will be produced from

$$= \frac{2 \times 109}{58} \times 55\ g\ \text{ethyl bromide}$$

As the yield is 85%, the actual ethyl bromide required

$$= \frac{2 \times 109}{58} \times 55 \times \frac{100}{85} = 243.2\ g$$

243.2 g of ethyl bromide will be produced from

$$= \frac{30}{109} \times 243.2 = 66.93\ g\ \text{ethane}$$

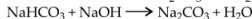As the yield is 90%, the actual ethane required

$$= 66.93 \times \frac{100}{90} = 74.37\ g$$

Volume of the ethane at NTP = $\frac{74.37}{30} \times 22.4$

$$= 55.5\ L$$

37. (a) : Since $NaHCO_3$ is an acid salt of H_2CO_3, it reacts with NaOH to form Na_2CO_3 and H_2O.

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

38. (c) : Si and P are in the 3rd period while C and N are in the 2nd period. Elements in 2nd period have higher electronegativities than those in the 3rd period. Since N has smaller size and higher nuclear charge than C, its electronegativity is higher than that of C. Similarly, the electronegativity of P is higher than that of Si. Thus the overall order is Si, P, C, N.

39. (b) : In N_2O_4 dimer, N–N bond is formed by pairing of odd electrons on each nitrogen atom in NO_2 and all four N–O bonds become equivalent.

40. (d) : $NaClO_4$ on hydrolysis gives NaOH and strongest $HClO_4$ acid as compared to other salts. Therefore pH of the solution will be lowest in this case.

■■

CBSE BOARD
SOLVED PAPER
2014
CLASS XII

Time : 3 hrs.   Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v)   Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. Give one example each of 'oil in water' and 'water in oil' emulsion.

2. Which reducing agent is employed to get copper from the leached low grade copper ore?

3. Which of the following is more stable complex and why?
   $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$

4. Write the IUPAC name of the compound :
   $$CH_3-CH-CH_2-COOH$$
   $$\qquad\ \ |$$
   $$\qquad\ \ OH$$
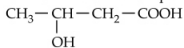
5. Which of the following isomers is more volatile: *o*-nitrophenol or *p*-nitrophenol?

6. What are isotonic solutions?

7. Arrange the following compounds in increasing order of solubility in water:
   $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

8. Which of the two components of starch is water soluble?

9. An element with density 11.2 g cm^{-3} forms a *f.c.c.* lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.
   (Given : $N_A = 6.022 \times 10^{23}$ mol^{-1})

10. Examine the given defective crystal.

A^+	B^-	A^+	B^-	A^+
B^-	0	B^-	A^+	B^-
A^+	B^-	A^+	0	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:
(i)   What type of stoichiometric defect is shown by the crystal?
(ii) How is the density of the crystal affected by this defect?
(iii) What type of ionic substances show such defect?

11. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K.
    (K_f = 5.12 K kg mol^{-1})

12. Define an ideal solution and write one of its characteristics.

13. Write two differences between 'order of reaction' and 'molecularity of reaction'.

14. Outline the principles behind the refining of metals by the following methods:
    (i) Zone refining method
    (ii) Chromatography method

15. Complete the following chemical equations:
    (i) $Ca_3P_2 + H_2O \rightarrow$
   (ii) $Cu + H_2SO_4(conc.) \rightarrow$

    OR

    Arrange the following in the order of property indicated against each set:
    (i) HF, HCl, HBr, HI – increasing bond dissociation enthalpy

(ii) H_2O, H_2S, H_2Se, H_2Te – increasing acidic character

16. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit?

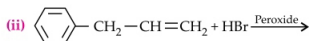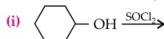17. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a)

(b)
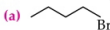
(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) inversion of configuration
(b) racemisation

18. Draw the structure of major monohalo product in each of the following reactions:

(i) OH $\xrightarrow{SOCl_2}$

(ii) $CH_2-CH=CH_2 + HBr \xrightarrow{Peroxide}$

19. (a) In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid.

20. (a) Draw the structures of the following molecules:
(i) $XeOF_4$
(ii) H_2SO_4

(b) Write the structural difference between white phosphorus and red phosphorus.
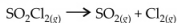
21. Account for the following:
(i) PCl_5 is more covalent than PCl_3.
(ii) Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.
(iii) The two O—O bond lengths in the ozone molecule are equal.

22. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.
(Given : log 4 = 0.6021, log 2 = 0.3010)

23. (i) Give two examples of macromolecules that are chosen as drug targets.

(ii) What are antiseptics? Give an example.

(iii) Why is use of aspartame limited to cold foods and soft drinks?

24. (i) Deficiency of which vitamin causes night-blindness?

(ii) Name the base that is found in nucleotide of RNA only.

(iii) Glucose on reaction with HI gives *n*-hexane. What does it suggest about the structure of glucose?

25. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.
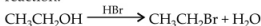After reading the above passage, answer the following questions:
(i) What values are shown by the students?

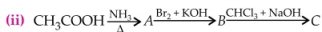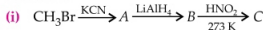(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a condensation or an addition polymer?

26. (a) Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

(b) Write the equation involved in Reimer—Tiemann reaction.

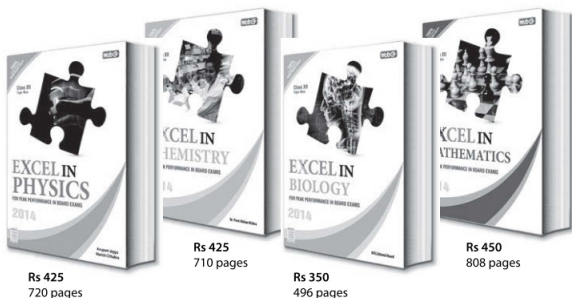27. Give the structures of *A*, *B* and *C* in the following reactions :

(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$

OR

How will you convert the following:
(i) Nitrobenzene into aniline
(ii) Ethanoic acid into methanamine

(iii) Aniline into *N*-phenylethanamide
(Write the chemical equations involved.)

28. (a) Define the following terms:
 (i) Limiting molar conductivity
 (ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} Ω^{-1} cm^{-1}.

OR

(a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu.

(b) Calculate the emf of following cell at 298 K:
Mg$_{(s)}$ | Mg^{2+}(0.1 M) || Cu^{2+}(0.01) | Cu$_{(s)}$
[Given : $E°_{cell}$ = + 2.71 V, 1 F = 96500 C mol^{-1}]

29. (a) How do you prepare:
 (i) K$_2$MnO$_4$ from MnO$_2$?
 (ii) Na$_2$Cr$_2$O$_7$ from Na$_2$CrO$_4$?

(b) Account for the following:
 (i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
 (ii) The enthalpy of atomization is lowest for Zn in 3*d* series of the transition elements.
 (iii) Actionoid elements show wide range of oxidation states.

OR

(i) Name the element of 3*d* transition series which shows maximum number of oxidation states. Why does it show so?

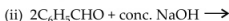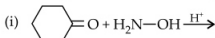**(ii)** Which transition metal of 3*d* series has positive $E°_{(M^{2+}/M)}$ value and why?

(iii) Out of Cr^{3+} and Mn^{3+}, which is stronger oxidizing agent and why?

(iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

(v) Complete the following equation:
MnO$_4^-$ + 8H$^+$ + 5e$^-$ $\longrightarrow$

30. (a) Write the product of the following reactions:

(i) ⬡=O + H$_2$N—OH $\xrightarrow{H^+}$

(ii) 2C$_6$H$_5$CHO + conc. NaOH $\longrightarrow$

(iii) CH$_3$COOH $\xrightarrow{Cl_2/P}$

(b) Give simple chemical tests to distinguish between the following pairs of compounds:
 (i) Benzaldehyde and benzoic acid
 (ii) Propanal and propanone

OR

(a) Account for the following:
 (i) CH$_3$CHO is more reactive than CH$_3$COCH$_3$ towards reaction with HCN.
 (ii) Carboxylic acid is a stronger acid than phenol.

**(b)** Write the chemical equations to illustrate the following name reactions:
 (i) Wolff—Kishner reduction
 (ii) Aldol condensation
 (iii) Cannizzaro reaction

SOLUTIONS

1. Oil in water emulsion : Milk
Water in oil emulsion : Butter

2. Scrap iron or H$_2$

3. [Co(*en*)$_3$]$^{3+}$ is more stable complex than [Co(NH$_3$)$_6$]$^{3+}$ due to chelate effect as it forms rings.

4. CH$_3$—$\overset{3}{\text{CH}}$—$\overset{2}{\text{CH}}_2$—$\overset{1}{\text{COOH}}$
|
OH
3-Hydroxybutan-1-oic acid
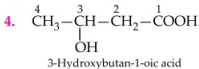
5. *o*-Nitrophenol forms intramolecular hydrogen bonding whereas *p*-nitrophenol forms intermolecular hydrogen bonding. So, *o*-nitrophenol is more volatile.

6. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

7. C$_6$H$_5$NH$_2$ < (C$_2$H$_5$)$_2$NH < C$_2$H$_5$NH$_2$

8. Amylose is water soluble and amylopectin is insoluble in water.

9. Given : d = 11.2 g cm^{-3}, Z = 4, a = 4 × 10^{-8} cm, M = ?, N_A = 6.022 × 10^{23} mol^{-1}

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$M = \frac{d \times a^3 \times N_A}{Z}$$

$$= \frac{11.2 \times (4 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4} = 108 \text{ g mol}^{-1}$$

10. (i) Schottky defect
(ii) Density of the crystal decreases.
(iii) This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.

11. Given : $w_2 = ?$, $M_2 = 256$ g mol^{-1}, $\Delta T_f = 0.48$ K
$w_1 = 75$ g, $K_f = 5.12$ K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

$$w_2 = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times 1000}$$

$$= \frac{0.48 \times 256 \times 75}{5.12 \times 1000} = 1.8 \text{ g}$$

12. Refer answer 18 and 20, Page 74.
(MTG Excel in Chemistry)

13. Refer answer 3, Page 167.
(MTG Excel in Chemistry)

14. Refer answer 4, Page 223. [Text Book Exercise with Answers] (MTG Excel in Chemistry)

15. (i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

(ii) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
(conc.)

OR

(i) $HI < HBr < HCl < HF$

(ii) $H_2O < H_2S < H_2Se < H_2Te$

16. Tetraamminedichloridochromium(III) ion. It exhibits geometrical isomerism.

17. (i) (b)

is chiral.

(a)

Br undergoes faster S_N2 reaction.

(ii) (a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction occurs with racemisation.

18. (i) Refer answer 5(i), Page 383.
(MTG Excel in Chemistry)

(ii)

19. (a) $\frac{x}{m} = kP^{1/n}$ ($n > 1$)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

where $\frac{x}{m}$ is the mass of gas adsorbed per gram of the adsorbent and P is pressure of gas.

(b) Lyophilic sols are reversible sols. These are quite stable and cannot be easily precipitated.

(c) Associated colloid : Soap
Multimolecular colloid : Gold sol

20. (a) (i) Refer answer 45(b)(ii), Page 284.
(MTG Excel in Chemistry)

(ii) Refer answer 71(ii), Page 288.
(MTG Excel in Chemistry)

(b) White phosphorus consists of discrete tetrahedral P_4 molecule.
Red phosphorus is polymeric, consisting of chains of P_4 tetrahedra linked togehter.

21. (i) Refer answer 1, Page 261.
(MTG Excel in Chemistry)

(ii) Iron reacts with hydrochloric acid to liberate hydrogen gas in the following way :

$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \uparrow$

Although Fe^{2+} gets easily oxidised to Fe^{3+} even in the presence of air but liberated hydrogen may react with available oxygen to form water and hence lowers the possibility of oxidation of Fe^{2+} to Fe^{3+}.

(iii) The two O—O bond lengths in the ozone molecule are equal as it is a resonance hybrid of two main forms:

22. The given reaction is

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

At $t = 0$ 0.4 atm   0   0

At time t $(0.4 - x)$ atm x atm x atm

Total pressure at time t will be

$P_T = (0.4 - x) + x + x$
$= 0.4 + x$
$x = (P_T - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x$
$= 0.4 - (P_T - 0.4)$
$= 0.8 - P_T$

At time ($t = 100$ s), $P_T = 0.7$ atm

$\therefore$ $p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$$k = \frac{2.303}{t} \log_{10} \frac{p_{SO_2Cl_2} \text{ (initial)}}{p_{SO_2Cl_2} \text{ (after reaction)}}$$

$$= \frac{2.303}{100} \log\left(\frac{0.4}{0.1}\right)$$

$$= \frac{2.303}{100} \times 0.6021 = 1.3 \times 10^{-2} \text{ s}^{-1}$$

23. **(i)** Refer answer 3, Page 616. [Text Book Exercise with Answers]   (MTG Excel in Chemistry)

   (ii) Refer answer 29 (ii), Page 626.
   (MTG Excel in Chemistry)

   (iii) Refer answer 16, Page 617.
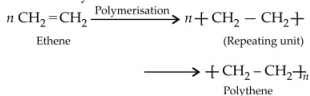   (MTG Excel in Chemistry)

24. **(i)** Vitamin A

   (ii) Uracil

   (iii) It suggests that all the six carbon atoms are linked in a straight chain.

25. **(i)** Students show awareness and responsibility towards the environment.

   (ii) Polymers which can be degraded by biological species like microorganisms are called biodegradable polymers. These polymers have functional group present in biopolymers and lipids.
   e.g. PHBV (poly-β-hydroxybutyrate-co-β-hydroxyvalerate)

   (iii) Polythene is an addition polymer that is formed by addition of ethene molecules.

   $$n\,CH_2\!=\!CH_2 \xrightarrow{\text{Polymerisation}} n + CH_2 - CH_2 +$$
   Ethene (Repeating unit)

   $$\longrightarrow + CH_2 - CH_2 \dfrac{}{}_n$$
   Polythene

26. **(a)** The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism, as shown below:

   Transition state

   Inversion of configuration takes place during the reaction.
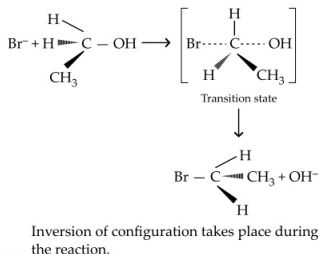
   (b) Refer answer 9(i), Page 424.
   (MTG Excel in Chemistry)

27. **(i)**
$$CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$
(A) (B)
$$\downarrow{273\ K}\ HNO_2$$
$$CH_3CH_2OH$$
(C)

   (ii)
$$CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2$$
(A)
$$\downarrow Br_2 + KOH$$
$$CH_3NC \xleftarrow{CHCl_3 + NaOH} CH_3NH_2$$
(C)   (B)

   OR

   (i)

   Nitrobenzene   Aniline
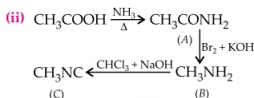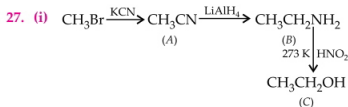
   (ii) Refer answer 5(i), Page 524.
   (MTG Excel in Chemistry)

   (iii)

   Aniline   *N*-Phenylethanamide (Acetanilide)
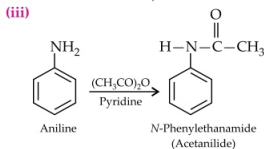
28. **(a)** (i) Refer answer 22, Page 124.
   (MTG Excel in Chemistry)

   (ii) Refer answer 55, Page 125.
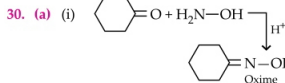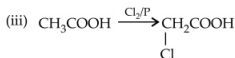   (MTG Excel in Chemistry)

   (b) Refer answer 50, Page 137.
   (MTG Excel in Chemistry)

   OR

   (a) Faraday's first law of electrolysis : The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
   Refer answer 54, Page 137.
   (MTG Excel in Chemistry)

   (b) The cell reaction can be represented as :
   $$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$$
   Given: $E^o_{cell} = +2.71$ V, $T = 298$ K
   According to the Nernst equation :
   $$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}_{(aq)}]}{[Cu^{2+}_{(aq)}]}$$
   $$= 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01} = 2.6805 \text{ V}$$
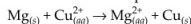
29. **(a)** (i) Potassium manganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3.
$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
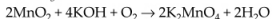
(ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.
$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$
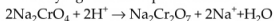
(b) (i) Refer answer 2, Page 311.
(MTG Excel in Chemistry)

(ii) Refer answer 2, Page 310.
(MTG Excel in Chemistry)

(iii) Refer answer 35, Page 321.
(MTG Excel in Chemistry)

OR

(i) Refer answer 3, Page 310.
(MTG Excel in Chemistry)

(ii) Refer answer 4, Page 310.
(MTG Excel in Chemistry)

(iii) Refer answer 51(ii), Page 331.
(MTG Excel in Chemistry)

(iv) Europium (Eu) is well known to exhibit +2 oxidation state due to its half-filled f orbital in +2 oxidation state.

(v) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

30. **(a)** (i)

(ii) $2C_6H_5CHO + conc.\ NaOH$
$$\longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

(iii)

(b) (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test. Benzoic acid will give effervescence with $NaHCO_3$ but benzaldehyde will not react.

(ii) Refer answer 13(i), Page 472.
(MTG Excel in Chemistry)

OR

(a) (i) It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to carbonyl carbon.

(ii) Refer answer 52, Page 487.
(MTG Excel in Chemistry)

(b) (i) Refer answer 15(iii), Page 484.
(MTG Excel in Chemistry)

(ii) Refer answer 15(iv), Page 484.
(MTG Excel in Chemistry)

(iii) Refer answer 15(i), Page 484.
(MTG Excel in Chemistry)

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